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THE CHEMICAL NEWS, JANUARY 28, 1910

THE
CHEMICAL NEWS

AND
JOURNAL OF PHYSICAL SCIENCE.

WITH WHICH IS INCORPORATED THE "CHEMICAL GAZETTE."

A Journal of Practical Chemistry

IN ALL ITS APPLICATIONS TO
PHARMACY, ARTS, AND MANUFACTURES.

EDITED BY
SIR WILLIAM CROOKES, D.Sc., F.R.S., &c.

VOLUME C.—1909.

101579.
26/4/10.

LONDON:
PUBLISHED AT THE OFFICE, 16, NEWCASTLE STREET, FARRINGDON ST.,
E.C.

AND SOLD BY ALL BOOKSELLERS.

MDCCCIX.

LONDON:

PRINTED BY EDWIN JOHN DAVEY,
16, NEWCASTLE STREET, FARRINGTON STREET,
E.C.

THE CHEMICAL NEWS.

VOLUME C.

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No. 2588.—JULY 2, 1909.

DETERMINATION OF PHOSPHORIC ACID.*

GRAVIMETRIC MOLYBDATE METHOD
FOR THE INTERNATIONAL TRADE OF RAW PHOSPHATES.

Mode of Analysis.

FIVE grms. of the substance are covered by 50 cc. of aqua regia in a flask of about 500 cc. and evaporated to nearly the consistence of syrup for the elimination of silicic acid.

The remainder, which after cooling will be approximately solid, is taken up by 10 cc. of nitric acid, specific gravity of 1.2, and 50 cc. of water, and boiled.

After cooling fill up to 500 cc. and filter.

50 cc. of the filtrate = $\frac{1}{4}$ gm. of the substance, are treated with an ample quantity of molybdic solution (at least 100 cc. for 0.1 gm. P_2O_5 —when the strength is greater take relatively more) and are digested on a water-bath for an hour at 50° C.

After sufficient standing filter through a small tight filter. The filtrate is to be examined by addition of new molybdic solution, warming to 60° C., and standing for twelve hours for the completeness of precipitation.

The remainder is washed by repeated decantations with a solution of ammonium nitrate containing nitric acid till calcium disappears. Five times washing with 20 cc. each time will be sufficient. (The calcium test is made by addition of 1 cc. of wash-water with a little sulphuric acid and 2 cc. of alcohol; there should be no turbidity).

The remainder in the beaker-glass is dissolved in about 80 to 100 cc. of ammonia of 2½ per cent and filtered on the same filter, and washed out five or six times with hot water. By this manipulation the volume of the filtrate may be increased 130 to 150 cc.

Then the solution of the yellow precipitate is warmed to 60 or 80° C., and immediately the phosphoric acid is precipitated with 20 cc. neutral magnesia mixture drop by drop and with constant stirring.

After standing at least four hours, or stirring for half an hour and a short sedimentation, filter it and wash out with ammonia of 2½ per cent till chlorine cannot be detected.

The filter and the precipitate together are brought into a crucible of platinum (if a Gooch's crucible, dry the precipitate before in the crucible), then ignite in such a way that the filter is carbonised without flame, ignite the crucible over the blast-lamp or crucible-furnace for five minutes, and weigh after cooling. The igniting must be repeated till the weight is constant.

On crushing the ignited residue it should be quite white throughout.

Factors for Conversion.

From $Mg_2P_2O_7$ to P_2O_5 : 0.63780.

From P_2O_5 to $Ca_3P_2O_8$: 2.185.

Determination of Moisture.

The determination of moisture in the sample for calculation of the strength in tribasic phosphate of lime in the dried matter is made at 100° C. to constant weight.

Preparation of the Solutions.

1. *Aqua regia*.—Three parts hydrochloric acid, specific gravity 1.12; one part nitric acid, specific gravity 1.2.

2. *Solution of Molybdate of Ammonium*.—150 grms. of molybdate of ammonium are to be dissolved in 500 cc. of hot water, and 400 grms. of nitrate of ammonium are separately dissolved in water; these two solutions are to be mixed and filled up to 1000 cc.

The mixture is poured immediately into 1000 cc. of nitric acid, specific gravity 1.2, allowed to stand twelve hours at about 60° C., and filtered. Warming the solution is considered not necessary, besides the same effect may be entirely attained by letting stand during twenty-four hours. Furthermore, it must be noticed that by prolonged standing the strength of the solution in molybdic acid may diminish by precipitation of molybdic acid.

3. *Wash Fluid for the Precipitate of Molybdate*.—Thirty-two parts of nitric acid, specific gravity 1.2, and 50 grms. ammonium nitrate are to be filled up to 1000 cc. The ammonium nitrate is to be examined for the absence of phosphoric acid.

4. *Ammonia of 2½ per cent*.—Five parts of ammonia of 25 per cent, specific gravity 0.91, and forty-five parts of water. Ammonia is to be examined for its purity; for instance, Pb absence.

5. *Neutral Magnesia Solution*.—50 grms. of $MgCl_2 \cdot 6H_2O$ and 150 grms. of NH_4Cl ; dissolve them in 1000 cc. of water.

Action of Phosphorus Haloids on Platinum Metals. —W. Strecker and M. Schurigin. —By the action of phosphorus trichloride and pentachloride on iridium a compound of formula IrP_3Cl_{12} or $IrCl_3 \cdot 3PCl_3$ is obtained, and the analogous compound with bromine may be prepared similarly. Under the same conditions ruthenium yields compounds $Ru_2P_3Cl_{19}$ and $Ru_2P_5Br_{19}$. With palladium a less stable compound $PdCl_2 \cdot PCl_3$ is formed. Rhodium and osmium give no compounds with phosphorus haloids, rhodium metal when heated with PCl_5 yielding $RhCl_3$, while with osmium no reaction occurs. —*Berichte*, xlii., No. 8.

* Proposed at the Seventh International Congress of Applied Chemistry at London, May 26 and 27, 1909. Reporter, Dr. ULLMANN.

NOTE ON THE RESULTS OF COOLING
CERTAIN HYDRATED PLATIN-CYANIDES IN
LIQUID AIR.*

By J. EMERSON REYNOLDS, M.D., Sc.D., F.R.S.

In the course of Sir James Dewar's important low-temperature researches he made an interesting and significant observation with a salt which had been supplied to the Laboratory of the Royal Institution as "Lithium Platinocyanide" (see *Proc. Royal Institution* for 1895, p. 667). When this nearly white crystallised substance was cooled in liquid air it assumed a distinct *red* colour, which did not persist at ordinary temperatures, the material resuming its usual appearance. Sir James was so good as to give the writer a portion of the salt for examination, as it seemed desirable to seek for some explanation of the remarkable colour change observed.

On repeating the above-mentioned experiment several times with one and the same portion of Sir J. Dewar's specimen it was subsequently found that the substance gradually lost the property of becoming red in liquid air, and assumed instead a marked *yellow* colour, which was retained at ordinary temperatures. This additional phenomenon has also to be explained, as it is presumably connected with that first observed.

Chemical examination of the Royal Institution specimen led to the conclusion that it was a mixture of the hydrated chloride, cyanide, and sulphate of lithium with a platin-cyanogen salt of lithium, and that the proportion of the latter compound present was small.

The percentages of platinum and of lithium were directly determined in the R.I. specimen, and found to be—

Platinum	1·82
Lithium	9·56

Hence the percentage of platinum compound present could not exceed 5 per cent of the mixture of salts. When this specimen was examined under a microscope some minute red specks were seen, and these minute particles deepened much in tint when the material was cooled in liquid air. The general red coloration of the mass at the same time indicated that the platinum colour-producing compound was also diffused through the salts in a state of solid solution.

The separation and identification of a small amount of a platin-cyanide in much saline material is not very satisfactory, hence the method of comparison was adopted. It seemed highly probable, having regard to all the circumstances, that the question to be decided was whether the compound present was a platinocyanide or one of the much less known platinicyanides—the presumption being, of course, rather in favour of the former.

With a view to this comparison I prepared afresh some pure lithium platinocyanide, and obtained the salt in fine grass-green crystals when fully hydrated. On completely analysing these crystals they gave data agreeing well with the formula $\text{Li}_2\text{Pt}(\text{CN})_4 \cdot 5\text{H}_2\text{O}$.

When cooled in liquid air this salt did *not* alter materially in colour—its green tint simply became paler after prolonged immersion. Even when previously diffused through hydrated lithium chloride, and the mixture cooled as before, it merely assumed a somewhat more yellow shade; but neither by cold nor heat did the pure material, or the mixture, become *red* on dehydration. It was therefore evident that the platinum compound present in the R.I. specimen was not a platinocyanide of lithium, and was probably a platinicyanide of the same base—the latter differing from the former in containing one more cyanogen group.

Happening to have in my collection a finely-crystallised specimen of lithium platinicyanide, its exact composition was then ascertained by direct analysis, and was found to be represented by the formula $\text{Li}_2\text{Pt}(\text{CN})_5 \cdot 2\text{H}_2\text{O}$. Hence

the material was ready to hand for carrying out the further comparison. This compound is, however, of a full *orange red* colour, at ordinary temperatures, and when cooled in liquid air becomes a magnificent *ruby-red* which does not alter on prolonged cooling. These observations did not, at first, seem to help much toward the end in view, but a careful study of the variations in hydration of the platinicyanide cleared away all further difficulty.

The orange-red di-hydrated crystals easily dissolve in water, and form a colourless solution. When this solution is cautiously evaporated at 40° to 50° to the crystallising-point and then quickly cooled to 15°, long *colourless* needle-like crystals separate which exhibit a slight lavender fluorescence. These crystals, when collected and quickly dried by pressure, were found to include $3\text{H}_2\text{O}$, i.e., one more molecule of water of crystallisation than the red salt. This colourless tri-hydrate easily parts with one molecule of water, and becomes the *red di-hydrate* either by heat or when the colourless crystals are cooled in liquid air. In the latter case, very rapid cooling always gave some *yellow* material in addition to the red substance, but when the reduction in temperature was carried out very slowly the red compound only was produced.

Further, when the orange-red crystals of the di-hydrated salt were very carefully heated until one of the remaining molecules of water was driven off, a *yellow* substance remained, which latter, if exposed to moist air, speedily resumed water, and became red again. I found, however, that a persistent yellow mono-hydrate could be obtained by adding to a colourless aqueous solution of the tri-hydrate a small proportion of an indifferent but highly hydrated salt—sodium sulphate—then evaporating to dryness, and gently heating the residue. The red stage of dehydration was quickly passed, and a persistent pure yellow coloured product remained, recalling in appearance the yellow substance which results from the quick cooling of the pure substance, as noted above, and also the product of the repeated cooling and thawing of the R.I. specimen, as mentioned at the beginning of this note.

Finally, when the pure platinicyanide was sufficiently heated, the last molecule of water of crystallisation was driven off, and a *white* anhydrous substance remained. It is, therefore, comparatively easy to obtain the following compounds by the means above indicated:—

$\text{Li}_2\text{Pt}(\text{CN})_5$	White
$\text{Li}_2\text{Pt}(\text{CN})_5 \cdot \text{H}_2\text{O}$	Yellow
$\text{Li}_2\text{Pt}(\text{CN})_5 \cdot 2\text{H}_2\text{O}$	Orange-red
$\text{Li}_2\text{Pt}(\text{CN})_5 \cdot 3\text{H}_2\text{O}$	Colourless

NOTE.—These formulæ should probably be doubled, but it is unnecessary to do so here, as the simpler expressions serve equally to represent the essential variations.

These variations of colour with degrees of hydration are doubtless to be connected with the differences in arrangement of the water molecules in the greater crystalline molecules, and their consequent effects on light.

The study of these hydrates evidently supplies the interpretation of the phenomena observed on cooling the Royal Institution specimen repeatedly in liquid air. The mixture of hydrated chloride, cyanide, and sulphate of lithium used included rather less than 5 per cent of lithium platinicyanide, which was chiefly in the tri-hydrated colourless condition. When the temperature of the mixture was reduced in liquid air, one molecule of water quickly separated, and the *red* di-hydrated salt was formed; but on warming up to the ordinary temperature, the colourless tri-hydrate was reproduced. The other hydrated lithium salts present are doubtless simultaneously dehydrated at the low temperatures reached, although these changes cannot be directly recognised as they are unaccompanied by colour alteration. In rapid cooling of the mixed (or even of the pure) material in liquid air a little of the yellow mono-hydrate is always formed, and, as already noted, this rehydration of the yellow substance is singular

* A Paper read before the Royal Society, April 29, 1909.

inhibited when neutral salts are present which are themselves avid of water, so that frequent alternations of cooling and warming gradually lead to the complete conversion of the platinum compound into the persistent yellow mono-hydrate.

The facts observed regarding the chemical changes of lithium platinyanide hydrates not only serve to explain the phenomena noted on cooling the R.I. specimen to temperatures between -180° and -200° , but also indicate that the study of graduated dehydration of coloured salts at low temperatures may present considerable advantages, as compared with that of similar salts under the more completely disintegrating effects of heat.

CONCERNING CERTAIN ORGANIC ACIDS AND ACID ANHYDRIDES AS STANDARDS IN ALKALIMETRY AND ACIDIMETRY.

By I. K. PHELPS and L. H. WEED.

In a former paper (*Am. Journ. Sci.*, xxiii., 211) from the Kent Chemical Laboratory of Yale University it has been shown that, with cochineal as an indicator, succinic acid may be used as a standard for a decinormal ammonium hydroxide solution quite as accurately as may a decinormal solution of hydrochloric acid, the standard of which is determined gravimetrically as the silver chloride. In this paper results are given which show that, in presence of phenolphthalein as an indicator, pure sodium hydroxide in solution and also pure barium hydroxide in solution may be determined similarly with succinic acid, succinic anhydride, malonic acid, benzoic acid, phthalic acid, and phthalic anhydride as standards. And, further, it is shown that these organic acids and acid anhydrides react with these alkaline solutions so that each may be used as a standard in acidimetry and alkalimetry with the same exactness that is found when these alkaline solutions are titrated in the well established manner with decinormal hydrochloric acid, standardised gravimetrically as silver chloride.

For the work given here a solution of hydrochloric acid was made up approximately decinormal by diluting the chemically pure acid of commerce in the usual manner. The exact strength of the hydrochloric acid solution was determined by precipitating definite amounts of it in a platinum dish in some cases, and in a glass beaker in others, by an excess of silver nitrate in presence of a few drops of dilute nitric acid. In each case the precipitate of silver chloride was allowed to stand for twenty-four hours before filtering on a weighed asbestos felt in a perforated platinum crucible. The volume in which the silver chloride was precipitated was such that after the precipitation was made it amounted to about 250 cc.

The sodium hydroxide solution was made up to correspond approximately to the hydrochloric acid solution by diluting with distilled water, freshly boiled, pure sodium hydroxide prepared by the action of water vapour on metallic sodium according to the method of Küster (*Zeit. Anorg. Chem.*, xli., 474). The barium hydroxide was prepared pure by crystallising twice commercial barium hydroxide out of hot water, washing the crystals after each purification with alcohol. A solution, approximately decinormal, was made by dissolving these crystals in a suitable amount of water and filtering into a closed bottle before diluting with freshly boiled distilled water. Both the sodium hydroxide solution and the barium hydroxide solution were kept in closed bottles, each connected with a three-way stoppered burette in the usual manner. These solutions were protected from the action of carbon dioxide in the air by soda-lime tubes.

In all the experiments recorded in the tables given below definite portions of the organic acids and acid anhydrides in most cases were treated with distilled water, and the solution of sodium hydroxide or barium hydroxide was

TABLE I.

No.	Succinic acid. Grm.	Succinic anhydride. Grm.	HCl value of NaOH used. Grm.	HCl value of BaO ₂ H ₂ used. Grm.	Theory in terms of HCl. Grm.	Error in terms of HCl. Grm.
1.	0.2000	—	0.1236	—	0.1235	+0.0001
2.	0.2000	—	0.1238	—	0.1235	+0.0003
3.	0.2000	—	0.1237	—	0.1235	+0.0002
4.	0.2000	—	0.1236	—	0.1235	+0.0001
5.	0.2000	—	0.1236	—	0.1235	+0.0001
6.	0.2000	—	0.1237	—	0.1235	+0.0002
7.	0.2000	—	0.1237	—	0.1235	+0.0002
8.	0.2000	—	0.1237	—	0.1235	+0.0002
9.	0.2000	—	0.1237	—	0.1235	+0.0002
10.	0.2000	—	0.1237	—	0.1235	+0.0002
11.	0.2000	—	—	0.1238	0.1235	+0.0003
12.	0.2000	—	—	0.1237	0.1235	+0.0002
13.	0.2000	—	—	0.1235	0.1235	—
14.	0.2000	—	—	0.1236	0.1235	+0.0001
15.	—	0.2000	0.1458	—	0.1458	—
16.	—	0.2000	0.1458	—	0.1458	—
17.	—	0.2000	0.1459	—	0.1458	+0.0001
18.	—	0.2000	0.1458	—	0.1458	—
19.	—	0.2000	—	0.1457	0.1458	-0.0001
20.	—	0.2000	—	0.1456	0.1458	-0.0002
21.	—	0.2000	—	0.1459	0.1458	+0.0001
22.	—	0.2000	—	0.1458	0.1458	—

TABLE II.

No.	Malonic acid. Grm.	HCl value of NaOH used. Grm.	HCl value of BaO ₂ H ₂ used. Grm.	Theory in terms of HCl. Grm.	Error in terms of HCl. Grm.
1.	0.2000	0.1404	—	0.1402	+0.0002
2.	0.2000	0.1403	—	0.1402	+0.0001
3.	0.2000	0.1402	—	0.1402	—
4.	0.2000	0.1401	—	0.1402	-0.0001
5.	0.2000	—	0.1401	0.1402	-0.0001
6.	0.2000	—	0.1400	0.1402	-0.0002
7.	0.2000	—	0.1402	0.1402	—
8.	0.2000	—	0.1400	0.1402	0.0002

TABLE III.

No.	Benzoic acid. Grm.	HCl value of NaOH used. Grm.	HCl value of BaO ₂ H ₂ used. Grm.	Theory in terms of HCl. Grm.	Error in terms of HCl. Grm.
1.	0.2000	0.0598	—	0.0597	+0.0001
2.	0.2000	0.0599	—	0.0597	+0.0002
3.	0.2000	0.0597	—	0.0597	—
4.	0.2000	0.0598	—	0.0597	+0.0001
5.	0.2000	—	0.0598	0.0597	+0.0001
6.	0.2000	—	0.0597	0.0597	—
7.	0.2000	—	0.0597	0.0597	—
8.	0.2000	—	0.0597	0.0597	—

TABLE IV.

No.	Phthalic acid. Grm.	Phthalic anhydride. Grm.	HCl value of NaOH used. Grm.	HCl value of BaO ₂ H ₂ used. Grm.	Theory in terms of HCl. Grm.	Error in terms of HCl. Grm.
1.	0.2000	—	0.0880	—	0.0878	+0.0002
2.	0.2000	—	0.0880	—	0.0878	+0.0002
3.	0.2000	—	0.0879	—	0.0878	+0.0001
4.	0.2000	—	0.0878	—	0.0878	—
5.	0.2000	—	—	0.0876	0.0878	-0.0002
6.	0.2000	—	—	0.0877	0.0878	-0.0001
7.	0.2000	—	—	0.0878	0.0878	—
8.	0.2000	—	—	0.0879	0.0878	+0.0001
9.	—	0.2000	0.0986	—	0.0985	+0.0001
10.	—	0.2000	0.0985	—	0.0985	—
11.	—	0.2000	0.0986	—	0.0985	+0.0001
12.	—	0.2000	0.0987	—	0.0985	+0.0002
13.	—	0.2000	—	0.0986	0.0985	+0.0001
14.	—	0.2000	—	0.0985	0.0985	—
15.	—	0.2000	—	0.0986	0.0985	+0.0001
16.	—	0.2000	—	0.0987	0.0985	+0.0002

introduced into these solutions by carefully drawing from the burette until the appearance of colour in the solution, due to the presence of phenolphthalein as indicator, showed the reaction to be complete. In a few cases the treatment was special, as is described.

Pure succinic acid was obtained by boiling succinic ester, whose purity was established by the fact that it distilled within one-fifth of a degree, on a return condenser for four hours with water containing a few drops of nitric acid. This solution was evaporated to crystallisation and the solid product, after the removal of the mother-liquor by filtering, was re-crystallised from distilled water. After these crystals had dried in the open air to constant weight it was found that on standing over sulphuric acid in a desiccator the weight remained unchanged. For the preparation of succinic anhydride, commercial succinic acid was treated with an excess of acetyl chloride and heated on a water-bath with a return condenser at 60° as long as bubbles of gaseous hydrochloric acid were evolved from the liquid. The material, which separated out on cooling, was re-crystallised from ethyl acetate. These crystals of succinic anhydride were then washed with absolute alcohol and were dried to constant weight over sulphuric acid in a desiccator.

The succinic acid used in experiments 6, 7, and 8 of Table I. had been dried for more than a year in a desiccator containing sulphuric acid, while that used in experiments 9 and 10 of the same table had been dried for the same length of time over calcium chloride in a desiccator. It is evident from these experiments that succinic acid dried in desiccators over sulphuric acid or calcium chloride for long periods of time is unaffected.

Owing to the considerable length of time that is taken by succinic anhydride to dissolve in water even in the presence of some alkali, experiments 20 and 22 of Table I. were slightly modified. In these the solution was heated until the anhydride completely dissolved before any of the alkaline hydroxide was added.

Malonic acid was prepared pure by heating for some hours between 50° and 60° on a return condenser malonic ester, which boiled between limits of two-tenths of a degree with water in the presence of a few drops of nitric acid. The volume was then concentrated, keeping the temperature of the solution below 60° until crystallisation began, the crystals filtered off and re-crystallised out of boiling water. The pure malonic acid was then allowed to come to constant weight over sulphuric acid in a desiccator.

To obtain pure benzoic acid benzoic ester was treated with sodium hydroxide in excess, and acidified with hydrochloric acid. The benzoic acid thus precipitated was crystallised twice from water and dried to constant weight in a desiccator over sulphuric acid.

In all of the experiments in Table III. alkali in amount nearly sufficient to neutralise the acid was run into the flask, which was then heated. This aided materially in securing the solution of the benzoic acid in the water and did not necessitate raising the solution to the boiling-point.

Phthalic acid was prepared by boiling in distilled water some commercial phthalic anhydride. The solution was filtered while still hot; the crystalline product obtained on cooling was separated by filtration, air-dried, and finally dried to constant weight in a desiccator over sulphuric acid. The phthalic anhydride was prepared in a state of purity by distilling *in vacuo* the phthalic anhydride of commerce. The product obtained was dried to constant weight in a desiccator containing sulphuric acid.

In Table IV. experiments 2 and 8 alone were carried on at ordinary temperatures. In the other experiments in this table the titrations were all performed after heating the solution until the phthalic acid or the phthalic anhydride used had entirely dissolved.

It is evident from the results recorded in the four tables that succinic acid, succinic anhydride, malonic acid, benzoic acid, phthalic acid, and phthalic anhydride may

be used with great exactness as standards for decinormal solutions of sodium hydroxide and of barium hydroxide. As a standard for a solution of barium hydroxide these organic acids and acid anhydrides are even more accurate in our experience than the determination of the barium hydroxide solution gravimetrically as the barium sulphate. In the various tables are given results which show the accuracy with which barium hydroxide may be standardised by the different organic substances when compared with the standard of decinormal hydrochloric acid established as the silver chloride. This same solution of the barium hydroxide which gave a value of 0.006396 grm. per cubic centimetre in terms of hydrochloric acid when standardised against the organic acids and acid anhydrides, gave a value of 0.006430 grm. per cubic centimetre in terms of hydrochloric acid when standardised by precipitating and weighing as the barium sulphate by the usual procedure for the determination of barium.

As standards in alkalimetry and acidimetry these organic acids and acid anhydrides, in pure state, are equally as accurate as the best previous standard—hydrochloric acid determined gravimetrically as the silver chloride. The most serviceable of these organic substances tested are those most readily soluble in water—succinic and malonic acids—although they are no more accurate than the other organic acids and acid anhydrides, as is shown by the results given in the tables. Since these substances can be readily prepared in a known state of great purity, their serviceability as most accurate standards is evident.—*American Journal of Science*, xxvi., p. 138.

THE USE OF BAKELITE FOR ELECTRICAL AND ELECTRO-CHEMICAL PURPOSES.*

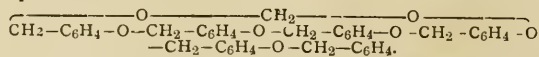
By L. H. BAEKELAND, Sc.D.

In my first paper on Bakelite read before the American Chemical Society, I have set forth the theoretical reasons why we may consider Bakelite C., or the final product, as a polymerised compound anhydride of a phenol-alcohol and methylenglycol (see *Journ. Indust. and Eng. Chem.*, March, 1909, p. 149; *Electrochem. and Met. Ind.*, March, 1909, p. 111; *CHEMICAL NEWS*, xcix., 200).

I have explained then and there how I have succeeded in producing this compound through indirect synthesis by the action of oxybenzyl alcohol on formaldehyde as well as by direct action of phenols on formaldehyde. The latter method is the more available one for practical purposes, and consists in heating under proper conditions a mixture of phenols and formaldehyde in presence of a catalytic agent, preferably small amounts of bases or alkaline substances. According to the conditions of operating, I have succeeded in carrying out the process in three phases, designated as A, B, and C.

A is the "initial product of condensation" produced by elimination of water, and contains probably one or more hydroxyl groups in its molecule.

B is the so-called "intermediate condensation product," a higher anhydride evolved by further elimination of water. In the case of ordinary phenol, we then have oxybenzyl-methylenglycol anhydride, the formula of which may be represented as—



C is the polymer of B and can be represented by $n(\text{C}_{43}\text{H}_{38}\text{O}_7)$, or its homologues in case the other members of the phenol series be used.

It is the final condition in the Bakelite process. This product C is characterised by the following properties:—

* A Paper presented at the Fifteenth General Meeting of the American Electro-chemical Society at Niagara Falls, Canada, May 6th to 8th, 1909.

It is a hard structureless mass, which may be prepared in transparent or in opaque condition; its colour varies from that of colourless glass to amber colour or dark ruby or brown. It is harder than shellac, hard rubber, or celluloid, but misses the flexibility of the two latter substances, and this is its main defect. On the other hand, it withstands all solvents and most chemicals, resists boiling water, steam, and superheated steam and oils. Heating does not melt it, nor even soften it to any serious extent. Boiling concentrated sulphuric acid destroys it; so does concentrated nitric acid, but it withstands dilute sulphuric acid, hydrochloric acid, and chlorine. It can stand temperature of 300° C. and over. At the temperature of melting glass it chars and carbonises without entering into fusion. In its final condition it can be sawed, cut, bored, and turned on the lathe, but it can no longer be moulded for practical purposes. In other words, when it has acquired condition C it is no longer a true plastic, so that all operations of moulding or shaping must preferably be carried out in its earlier stages. In its final stage it is tasteless and odourless, and an excellent insulator of heat and electricity.

In cost of production it can very advantageously compete with any known plastic.

For all practical purposes we use A as raw material to start with. The latter is obtained in four varieties, each of which may be preferable according to the special purpose in view.

Extra thin liquid A is a thin liquid of great penetrating power, and therefore is best fit for impregnating such bodies which absorb liquids with some difficulty, as, for instance, wood.

Liquid A is another variety of which the consistency is about that of molasses syrup. It can be made considerably thinner by slight heating. Longer heating at 60° to 70° C. thickens it gradually so that it can become pasty; still longer heating at this temperature may convert it into B, which is no longer fusible, but still remains soft while hot.

Dissolved A is a mixture of A with a small amount of alcohol which can be further diluted to proper strength by the proper addition of alcohol. If an excess of alcohol be added to it, the whole dissolved mass may re-precipitate and separate itself in two layers: a lower viscous one, containing the precipitated A, and a supernatant thin liquid containing mainly the added alcohol. Acetone re-dissolves this precipitate. The alcoholic solution dries in about the same way as shellac varnish, but drying at ordinary temperatures, or even somewhat higher temperatures, does not bring the layer beyond the stage A; in other words, this varnish layer remains fusible and soluble. Only at relatively high temperatures and in presence of suitable amounts of catalytic agents does it transform finally in hard insoluble C. In all cases where the coating is rather thick, or where it is applied on porous surfaces like wood, it becomes absolutely essential to carry out the heating in a Bakeliser under suitable pressure as explained below so as to avoid air bubbles and blistering.

Solid A.—A brittle irregular, opaque, translucent, or transparent mass of about the consistency and brittleness of ordinary rosin or colophonium. It can be made in different degrees of hardness from a variety which melts at 40° C. or under, to a modification which melts only at 100° C. or over. If heated for a few hours at about 70° C., it slowly hardens more and more, then changes into B. The main characteristic of Solid A is that it still is fusible and soluble in caustic soda as well as in acetone or in a mixture of alcohol and acetone.

It can be easily ground to a fine powder, and mixed with any variety of fillers, and thus become very well suited for the manufacture of moulded objects.

Solid A at first sight resembles very closely B; it has the same appearance, is about of equal brittleness, but B if heated does no longer melt, although it softens and becomes rubber-like. Furthermore, B is insoluble in neutral solvents; acetone and phenol may swell it some-

what, but not dissolve it. How the valuable properties of A are utilised in practice we shall see later on.

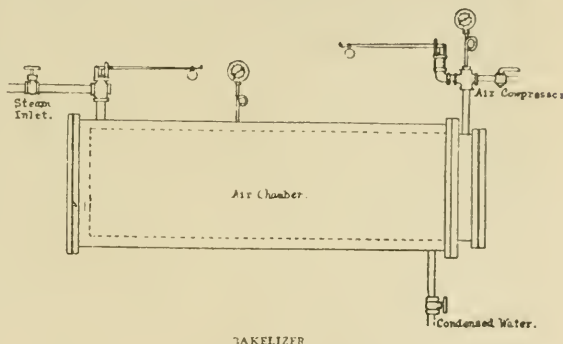
In the different modifications of the Bakelite process the aim in view is to produce the final product C; but in as far as C is no longer plastic, all forming, shaping, moulding, or mixing is carried out in the earlier stages.

This is accomplished either by transforming directly A into C in one single operation, or in other cases, specially in rapid moulding processes, it is found more convenient to change A into B, then remove B from the mould, and afterwards change it into C without the use of a mould. In some other case the moulding or shaping process is started from B, and the latter is then changed into C by the application of heat.

Whether stage C is arrived at directly from A or indirectly from B, the quickest result and the best product is obtained by heating at relatively high temperatures, say, 160° C. or over. But as at temperatures above 100° C., A dissociates into gaseous products, and causes the resulting mass to be porous and spongy, I found it necessary to heat under pressure. Without this precaution the resulting mass will be technically worthless.

If the heating occurs in closed moulds or closed vessels the so developed internal pressure may be sufficient to counteract the chemical dissociation which causes porosity.

In all other cases the heating should be conducted in a so-called Bakeliser as shown by sketch.



This is an apparatus consisting essentially of an inner chamber where the objects are placed, and in which, by means of a suitable pump, air can be compressed to 100 or 120 pounds; this pressure is maintained during the heating. A steam-jacket heats the chamber to a temperature of 140° to 180° C., equivalent to about 54 pounds to 150 pounds of steam.

The higher the temperature, the shorter will be the bakelising process, which converts everything into C.

In such cases where Bakelite is used in presence of substances which cannot stand such high temperatures, as, for instance, wood, wood-pulp, or paper, somewhat lower temperatures should be used, and the operation takes more time. All these conditions have to be adjusted after direct experiment for each different material. For substances like asbestos or other mineral fillers it does not matter if temperatures as high as 200° C. and very long bakelising be used.

The different applications of Bakelite can be divided summarily into block-working processes, impregnating processes, coating processes, and moulding processes.

In some cases one or more of these processes are carried out conjunctively.

Block-working.—This process suggests itself naturally to the mind, and can be carried out in many ways. The simplest manner is to heat a mixture of phenols and formaldehyde under pressure in presence of a condensing or catalytic agent, say a small amount of a base. But it is more advantageous to start with one of the varieties of A described above. The A may be simply poured in a mould or mixed first with pigments, colours, or suitable

filling materials; for instance, asbestos, clay, mica, bone-black, iron oxide, sawdust, wood-pulp, finely divided metals, mica, abrasives, graphite, &c., and thus produce an endless variety of compositions more or less suitable for certain special purposes. By heating the mess at 140—180° C. under suitably increased pressure, the whole solidifies to a solid block, which has the exact shape of the container, and can easily be removed therefrom because there is a slight shrinkage. The process may take from one to two or three hours according to the size of the block, the temperature, and the amount of base used. If organic fillers are used which are destroyed by too high temperatures, as, for instance, wood-pulp, then the minimum temperatures must be preferred, and the time of heating must be increased accordingly. No such restrictions exist for mineral fillers.

The so obtained blocks can now be sawed, cut, turned, polished, and shaped in about the same way as ivory or bone is handled.

For large blocks the following difficulty presents itself:—In the final act of polymerisation, the mass contracts in volume, and as it is rather difficult to carry out the heating in a sufficiently gradual manner, it may happen that the crust be transformed in C before the heat has made its full action felt in the centre. This may cause rents or cracks through the mass. Furthermore, C is very hard, and difficult to cut, saw, or turn. Therefore it is easier to simply continue the heating until stage B is reached, and then cut the latter to the proper shape; then B is submitted to further action of heat until it is changed into C.

I should mention that B while slightly warm is soft and somewhat elastic, and cuts about as easily as Swiss cheese, yet if heated further it does not liquefy nor change its original shape. The transformation of A into B does not need to be carried out under pressure. It may be accomplished simply by heating for a few hours, at temperatures not exceeding 70° C., any of the varieties of A, either in an air stove or in a water-bath. The progress of the reaction can be easily followed by the touch. The A will thicken more and more until it is no longer fusible, and feels elastic in about the same way as coagulated gelatin. When this stage is reached, B can be removed from its receptacle and be cut to proper shape, or the block can simply be cooled and stored away for future purposes. On cooling, B becomes hard and brittle, but if dipped in hot water it becomes soft again, and regains its former elasticity.

In order to change B into C it can be heated to proper temperature in a Bakeliser as described above. B is no longer attacked by hot water, as A is, and for that reason it may be simply heated in an ordinary autoclave containing water, in about the same way as rubber is vulcanised for dental purposes, with this difference, however, that higher temperatures should be used than are permissible in the rubber process.

Moulds are here entirely superfluous, and the objects so treated will retain perfectly their shape. Temperatures of 160° C. to 170° C. are quite suitable, but I have used with impunity temperatures as high as 200° C. and over.

I mention this fact for persons who are acquainted with rubber vulcanising, and who are inclined to carry out bakelising at too low temperatures or too short a time; indeed, "over-vulcanising" is a constant menace to the rubber manufacturer.

Plates, blocks, and objects of various sizes and dimensions may thus be manufactured easily, but this process, however simple, does not commend itself in such cases where large quantities of articles of the same size have to be produced. For such purposes it is much cheaper to mould in the press, which allows quick and accurate work, without further necessity of milling or machinery or polishing. How this is done is described under the heading of moulding processes.

Impregnating Processes.—Liquid A, specially in its extra thin variety, is readily absorbed by any porous materials.

ts penetrating power is far superior in this respect to varnish solutions, rubber solutions, or similar viscous or incompletely dissolved masses which have a tendency to merely stay on the surface notwithstanding the aid of high pressure.

If a piece of non-resinous soft wood, like bass wood or poplar wood, be immersed in extra thin liquid A, after a few hours it will be found that the wood has doubled or even tripled its former weight. The absorption of the liquid is accompanied by some swelling of the wood, and the latter becomes translucent on the edges, which shows that the interior of the individual wood-fibres is entirely filled. The same treatment can be given to unsized paper, paper-pulp, cardboard, asbestos, objects of cement, or plaster of Paris; in fact, to any material of a fibrous, cellular, or otherwise porous texture.

For such articles which absorb easily, regular liquid A can be used, although it is somewhat thicker; in this instance slight heating will render it more fluid. In other cases it becomes necessary to use extra thin liquid on account of its greater penetrating power. The addition of solvents like alcohol or others does not work well except in special cases, as, for instance, thin sheets of blotting-paper, because these solutions do not seem to penetrate as well; furthermore, the use of solvents introduces a new factor which retards the synthesis.

Resinous woods like pine are very difficult to impregnate. Bass, poplar, and similar woods, as well as unsized pulp board are easily impregnated by plain soaking, and this can be helped by the usual methods of injection under pressure. The preliminary use of a vacuum does not seem to be so advantageous from the fact that when liquid A enters the vacuum chamber it dissociates, evolving formaldehyde gas, and the liquid starts boiling and foaming violently. I found it much simpler to heat the substance that has to be impregnated at about 120° C. for several hours until all water and air is expelled, and then to immerse the objects, while they are still hot, into the liquid A, where they are left to soak; if more complete impregnation is desired, the force pump may be resorted to.

The impregnated material is now transferred to the Bakeliser and submitted there to final treatment.

It should be borne in mind that we have to deal here with chemical phenomena occurring in capillary spaces. Under the latter conditions chemical reactions are considerably retarded. The chemical dynamics here are much influenced by decreased mobility of the reacting molecules. For this reason it is necessary to heat longer than for ordinary conditions.

On the other hand, the capillary conditions depress at the same time, the tension of dissociation; this explains why wood or cement impregnated with liquid A can be heated at temperatures somewhat above 100° C., without applying pressure and yet not give a porous result. So under these special conditions a Bakeliser can be dispensed with by raising slowly the temperature from 70° C. to 130° C. But even then we have to guard against a considerable loss of formaldehyde vapours which are set free during the first period of heating, and which may prove a disturbing factor by altering too much the chemical composition of the impregnating material.

So that, after all, whenever heating in a Bakeliser is practicable, it ought to be preferred even if only for the fact that it will shorten the heating process very considerably.

It is advisable to supplement the treatment with a slow after-drying so as to expel any traces of water which may have been liberated during the synthesis.

In most instances it will be found that the impregnated objects have a dull appearance on the surface. Whether this be due to the fact that the pressure in the Bakeliser has forced the liquid inwards, or whether it has to be ascribed to surface evaporation, it can be easily remedied by applying a second superficial coat of thicker A.

The latter is best applied while the objects are still hot; this treatment will impart a very hard and very glossy surface.

Wood thus treated is not only much harder and stronger, but it has become rot proof, and is a better electrical insulator. It withstands dilute acid solutions and ordinary electrolytes. It can be used to excellent advantage for third-rail covers. Similar usages can be found for impregnated pulp board, cardboard, and asbestos board.

Asbestos paper or asbestos tissue impregnated with A or B makes an excellent packing material for gaskets, washers, and similar purposes.

In that condition it can be carried in stock indefinitely, either in the form of flat sheets or in ready-made sizes. As soon as this packing material is applied to a hot surface under pressure, the A becomes plastic, and moulds itself thoroughly over the surface, and is gradually transformed into hard permanent C.

In certain cases, the admixture of graphite or similar filling materials may prove advantageous.

(To be continued.)

BRUSSELS INTERNATIONAL AND UNIVERSAL EXHIBITION.

MAY TO OCTOBER, 1910.

Official Assistance to the British Exhibitor.

MANUFACTURERS all over the country are beginning to realise and appreciate the extraordinary amount of assistance offered to them by the British Government to enable them to make suitable exhibits at the Brussels International Exhibition next year. The Royal Commission appointed to take charge of the Exhibitions at Brussels in 1910, and at Rome and Turin in 1911, has studied exhaustive reports of executive work in other countries, and has also been at great pains in investigating the methods pursued at previous Exhibitions in which Great Britain participated. The result of all this work is shown in the untiring energy now being displayed by the Board of Trade officials in securing the many favourable considerations which should influence the British exhibitor.

The Royal Commission, which is presided over by H.R.H. the Prince of Wales, has its offices in Queen Anne's Chambers, Westminster, and the active official is Mr. U. F. Wintour, Secretary and Commissioner-General and Director of the Exhibitions Branch of the Board of Trade. This branch is to be a permanent office for the consideration of future and revision of past International Exhibitions in which Great Britain has been, or will be, concerned.

Every conceivable information required by proposed exhibitors can now be promptly given. Up to the present many instructive circulars and press paragraph matter have been issued, and the willing interest attracted of Chambers of Commerce everywhere in the country; while from the chiefs of the great railroads, the steam ship companies, and of every other important transport company, hearty assistance in the shape of cut-rates has been assured.

Position of the British Section.

The report of the Committee of Investigation showed most conclusively the many causes for the disinclination to exhibit and the general lack of enthusiasm in recent years on the part of the British manufacturer for International Exhibitions. They complained of lack of organisation, of isolation of exhibits, of unsuitable surroundings, of unwarrantable expense, of the necessity of costly personal supervision, of the decrease in the value of awards, and of several more defects and shortcomings which the Royal Commission will do its best to obviate, curtail, or amend, as is suitable in each case. At Brussels next year the British Government has secured perhaps the most prominent position in all the Exhibition for its section. Hitherto, owing to carelessness or tardiness, Great Britain has seen in nearly every instance all the good position secured prior to advancing her own claims; this time the

British representatives were prompt to seize on a primary choice. The British section amounts to 203,140 square feet, of which 150,640 square feet are in the Industrial Hall, and 52,500 square feet in the Machinery Hall. The amount of space covered, and certainly the positions secured, compare most favourably with the allotments to other countries. One great advantage lies in the fact that visitors must pass through the British Galleries before reaching the French, German, Italian, American, and other national sections, and the old proverb of "first impressions" holds good.

The main gallery running through the British section is 510 feet long by 98 feet wide, and there are four other parallel galleries 56 feet wide, which lend themselves to the formation of attractive courts for the display of the different classes of manufactures. At the end of the main gallery, furthest from the entrance, is a double staircase leading to a bridge which gives access to the French and other foreign sections.

The Isolation of British Exhibits.

In the Machinery Hall the portion allotted to Great Britain occupies the centre of the hall, and has easy access to the electric, steam, water, and gas mains, from which power can be obtained for showing all classes of machinery in motion. It is also intersected by three lines of rails which communicate directly with the Belgian State Railway system.

There will be no isolation of British exhibits; all will be shown together, appropriately grouped and arranged under the immediate supervision of officials of the Royal Commission. All the exhibitor has to do is to purchase the space he requires and see to the transportation, for which a variety of special facilities have been secured. The principal railway companies, for instance, have agreed to accord a reduction of 50 per cent on the usual rates for the conveyance of all unsold exhibits returned after the close of the Exhibition.

The Royal Commission officials will undertake the entire handling of the exhibitors' goods within the Exhibition; not only unloading and displaying on the space reserved, but storing all empty packing cases and reloading at close of Exhibition. With the exception of machinery and rolling stock, the exhibits of Great Britain will be grouped so as to form a complete national display of the various manufactures and products; and with a view to uniformity, the Royal Commission will undertake the entire decoration of the British section and provide all show cases, stands, platforms, and screens required by each individual exhibitor without further charge.

The importance of this determination to provide free show cases, &c., can be readily appreciated by quoting a paragraph from the report of the Board of Trade Committee. It seems that other Governments at previous International Exhibitions invariably insisted on a general scheme of decoration and uniformity of pattern in show cases. "In the British section," says the report, "no considered plan would as a rule appear to have been adopted in allotting the space to exhibitors of different classes of goods. Artistic pottery has been exhibited side by side with trouser stretchers, scientific instruments have been placed next to the exhibit of a theatrical wig-maker, and glassware of a highly decorative character has been surrounded by pyramids of empty bottles and syphons. In this manner the uneven quality of many of the exhibits has been accentuated and the general effect of the section spoilt. The decoration of the exhibits, moreover, appears to have been left almost entirely to the exhibitors themselves. Each exhibitor has provided his own show case, and has decorated his stand in the manner that pleased him best."

The Scheme of General Decoration.

In order to assist in attaining this desired and most necessary improvement, the scheme of decoration and grouping will be carefully explained to intending exhibitors, and every endeavour made to reconcile conflicting interests.

The internal fittings and the material used for lining must, of course, be at the expense of the exhibitor; but the attractive and harmonious design of the show cases, it is anticipated, will appeal most favourably alike to exhibitor and spectator.

Every care will be taken to prevent any deprivation of individual character from the exhibits, either by too close proximity or other unharmonising causes, and if an exhibitor prefers to use his own show cases, no objection will be made provided such show cases are sympathetic to the general scheme of decoration and surroundings. Designs of show cases and the proposed decorations will be on view at the offices of the Exhibitions' Branch of the Board of Trade at an early date.

In view of the great efforts which it is stated will be made by France, Germany, Italy, the United States, and certainly by Belgium itself, to give a most effective display of the most up-to-date machinery, the Royal Commission are desirous of assisting in every way to make the British machinery exhibit unrivalled. With that view the Commission will defray fifty per cent of the charges made by the Belgian Administration for the supply of steam, gas, and electricity, when used for showing machinery producing finished articles, or illustrating a process of manufacture. This should be a most welcome reduction of expense, judging by the complaints of costs made by machinery exhibitors at previous World's Fairs.

Another great convenience and saving of time and expense to machinery exhibitors has also been most thoughtfully considered by the Royal Commission. Exhibitors requiring foundations or shafting for machinery must provide them at their own cost, but can, upon sending to the offices of the Royal Commission drawings with metric measurements, have estimates obtained for them from Belgian contractors, and the work carried out under the superintendence of a competent engineer employed by the Royal Commission. No charge will be made to exhibitors for assistance rendered in this connection. Hitherto, machinery exhibitors have had to send their own constructors and engineers to superintend, frequently resulting in weeks of idle delay and unremunerative expense for expert artisans forced to await their turn. Estimates from a reliable contractor in Brussels, under the supervision of the Royal Commission, will be supplied on written request to the General Commissioner at Queen Anne's Chambers, and other estimates from equally reliable sources in Belgium can also be obtained. Crane power will be provided up to seven tons weight free of charge, and special facilities for handling heavier weights can also be secured if application be made.

A special catalogue of the British section will be made in English and French without charge to the exhibitor either for translation or insertion, and all necessary steps will be taken by the Belgian Government for the protection in Belgium of inventions, industrial designs, and trade marks shown at the Exhibition.

In regard to the question of dual language, the Royal Commission specially wishes to impress upon exhibitors the desirability of having their trade catalogues and price lists translated into French. Metric equivalents of the dimensions and weights of exhibits may often be given with advantage where such information is required, and the exhibitor's agent should be in a position to quote the purchase price in Belgian currency, inclusive of freight, custom duties, and other charges. The Customs Tariffs of the principal European countries will be filed in the exhibitors' reading room, together with the British Commercial Directories, a collection of Technical Dictionaries, and Telegraph Codes.

The report of the Committee on previous International Exhibitions deplores the fact that in several cases the attendants in charge of stalls at an Exhibition were unable to describe the goods exhibited in a correct or intelligible manner; in other cases their technical knowledge was often thrown away owing to their inability to speak any language but their own.

This statement clearly shows the importance of an active and capable attendant being able to speak French, and other languages perhaps, fluently and technically. The Royal Commission, however, will assist matters to a great extent by providing a special apartment in which exhibitors or their agents may conduct business and deal with their correspondence. A staff of interpreters, acquainted with French, German, and Italian, will also be available to afford any assistance and information that may be required.

In future articles the scope of the Exhibition will be described, the progress made in the buildings, the arrangements in regard to tariff, &c., the advantages of International Exhibitions in the opinion of the Royal Commission, the chief exhibits expected, the proposed fêtes and sports, and other interesting matter given which will be regularly communicated to us by the General Commission.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, June 17th, 1909.

Sir ARCHIBALD GEIKIE, K.C.B., President, in the Chair.

PROF. John Alexander McClelland was admitted into the Society.

Papers were read as follows, the Summaries here printed having been supplied by the author for use at the meeting:—

"On the Nature of the Hydrogen Flocculi on the Sun."

By PROF. G. E. HALE, For. Mem. R.S.

Photographs of the H_{α} line in the spectrum of the solar disc, made on Mount Wilson with high dispersion, were shown on the screen. The line appears as follows:—
1. A broad dark line, differing greatly in intensity and width in different regions of the sun. Except in eruptive or rapidly changing phenomena, the differences in width are not very marked.
2. Within the boundaries of the dark line a narrow single or multiple bright line is photographed in many parts of the sun. Sometimes the appearance resembles that of the calcium lines K_2 and K_3 —i.e., the bright line lying on its dark background is divided into two components by a central dark line. In other regions the bright line is divided into a larger number of components, varying in width and separation.

The images of dark hydrogen flocculi, on spectrohelio-graph plates taken with camera slit about equal in width to H_{α} , appear to be due, in the main, to local increase in the intensity of the dark line. In some parts of the sun, particularly those where the line is distorted, variations in the width of the line may also play an important part.

The increased intensity of the dark line is probably the result of increased absorption. Slides were shown to illustrate the fact that prominences at the sun's brink are frequently recorded as dark flocculi when photographed in projection against the disc.

The possible effects of anomalous dispersion were discussed, and photographs were exhibited of the same region of the sun, taken simultaneously with light from the red and violet edges of H_{α} . The similarity of these photographs apparently indicates that anomalous dispersion is not the prime factor in producing the hydrogen flocculi. Certain minor differences suggest, however, that it may perhaps play a secondary part in modifying their form.

"On the Origin of Certain Lines in the Spectrum of ϵ Orionis (Alnitam)." By Sir NORMAN LOCKYER, K.C.B., F.R.S., F. E. BAXANDALL, and C. P. BUTLER.

The star ϵ Orionis (Alnitam) is of great importance as offering a possible transition stage between the helium and bright line stars, and the only outstanding lines of unknown

origin were those at 4097, 4379·8, and a conspicuous double at $\begin{matrix} 4647\cdot6 \\ 4650\cdot8 \end{matrix}$.

In the case of 4097, the clue to the identification was obtained from a spark spectrum of chromium, showing local intensifications of certain lines at one of the poles. Two of these lines were found to be the previously-known silicon (IV.) lines, 4089, 4116, probably present as impurities in the fused chromium, while one of the remaining two lines was found to coincide with the ϵ Orionis line at 4097. These four lines are shown under various conditions in the plate, indicating the steps taken in tracing their origin to nitrogen.

In the spectrum of nitrogen under the special conditions which gave the above lines at 4097, 4103, another line was found at 4379·8, which was greatly strengthened in comparison with its intensity in the ordinary spark, and this line coincides with the unknown line in ϵ Orionis.

During the work on the above lines, one of the photographs taken of an alcohol spectrum showed abnormal intensifications on either side of the oxygen line 4649·2, suggesting the presence of a new double. The wave-lengths of the components of this double were determined as 4647·6, 4650·8, coinciding with the wave-lengths of the components of the strong double in ϵ Orionis. By a series of comparison photographs of spectra under varied conditions, the origin of the double was traced to carbon, and one of the strips of the plate (carbon spark in hydrogen) shows it quite isolated as it appears in the stellar spectrum. Further evidence of the validity of the identification is afforded by the peculiar nature of the components of the double.

"On Electric Induction through Solid Insulators." By Prof. H. A. WILSON, F.R.S.

This paper contains an account of a series of experiments on the variation of the capacity of ebonite and other condensers, with the time of charging and with the potential difference.

It is shown that the capacity of C after a time of charging t is given by the formula $C = C_0(1 + B \log(1 + \frac{t}{p}))$ where C_0 denotes the capacity when $t = 0$ and B and p are constants. In the case of ebonite at 30° C. this formula represents the results obtained to within one part in 2000. The values of the constants have been found for several substances at different temperatures. The capacity is shown to be independent of the potential difference within the limits of error.

It is shown that after the temperature of an ebonite condenser has been changed, then a very slow change in the capacity goes on which continues for more than 100 hours at constant temperature.

"The Effect of Pressure on the Band Spectra of the Fluorides of the Metals of the Alkaline Earths." By R. Rossi, B.Sc.

It was shown by A. Dufour that the band spectra of the fluorides of the alkaline earths show a marked Zeeman effect, and it was thought interesting to see whether these particular bands would also be displaced by pressure, for it is known that the cyanogen bands, which, like most bands, do not show a Zeeman effect, are not displaced by pressure.

The large 214-foot concave grating spectrograph of the Physical Laboratory of the Manchester University was used, and the bands of the fluorides of calcium, barium, and strontium were found to be shifted by pressure.

The order of magnitude of the displacement is about the same as for line spectra.

The components into which the bands are resolved are widened by pressure, and the linear relation between pressure and displacement found by former observers on line spectra seems to hold also for these bands.

There does not seem to be any evident relation between the magnitudes of the Zeeman and pressure-shift effect in the case of these bands.

"The Ionisation produced by an α -Partiele." By Dr. H. GEIGER.

The aim of the experiment was an accurate determination of the number of ions produced by an α -particle when completely absorbed in air. The most direct way to find the number of ions would be to measure the whole ionisation produced by the α -particles from a known quantity of radium C. Since it is, however, practically impossible to obtain the saturation current due to the α -particles at atmospheric pressure it was necessary to adopt an indirect method. This method was briefly as follows:—The ionisation due to the whole number of α -particles expelled from a known quantity of radium C was measured at a low pressure allowing only a small definite portion of the range of each α -particle to be effective. The ratio of the ionisation produced within this small portion of the range to the ionisation produced along the whole path was then found from an accurate determination of the ionisation curve.

It was found that the number of ions produced in air by an α -particle from radium C along its whole path is $2\cdot37 \times 10^5$. Since the α -particles from different radioactive products differ only in their initial velocity, it was possible by the aid of the ionisation curve of radium C to calculate the number of ions produced by the other products.

"On a Diffuse Reflection of α -Particles." By Dr. H. GEIGER and E. MARSDEN.

It was observed that a diffuse reflection takes place when α -particles are incident on a plate. The reflected particles were counted by the scintillations produced on a zinc sulphide screen.

The effect was found to vary with different metals as reflectors; the amount of reflection being approximately proportional to the atomic weight of the reflecting substance. Using different numbers of thin gold foils as reflectors it was found that the reflection was a volume effect, and thus similar to the reflection of β -particles. Taking a measured quantity of radium C as source, and using a plate of platinum as reflector, it was found that, of the incident α -particles, about 1 in 8000 suffers reflection.

"The Decay of Surface Waves produced by a Superposed Layer of Viscous Fluid." By W. J. HARRISON, B.A.

An estimate is obtained of the effect of a thin layer of viscous liquid on the decay of waves at the surface of a slightly viscous liquid. The period equation for the motion is of the fourth degree, and has two real and two complex roots in the case of waves of less than a certain length, and four complex roots in the case of waves of greater length. The real roots correspond to dead-bent modes, the complex roots to propagated modes. No general expression of any use can be obtained for the damping, but the equation can be solved numerically in any particular case. In the paper the velocity of propagation and the modulus of decay are given for waves of length 2, 5, 10, 20 cm. at the surface of mercury on which is superposed a layer of glycerin 1 mm. in depth. An estimate is also obtained for the damping when the wave-length is small compared with the depth of the layer. Two other problems in the decay of surface waves are discussed.

"The Passage of Electricity through Gaseous Mixtures." By E. M. WELLISCH, M.A.

i. An experimental method (based on Langevin's method) has been devised in order to ascertain whether there are two distinct mobilities for the positive or for the negative ions produced by Röntgen rays in a mixture of two gases, or of a vapour and a gas.

ii. No evidence was found of the existence of the two distinct mobilities; accordingly it is necessary to conclude that the motion of the ion through the medium must involve a mechanism of a character such as to produce a statistical average.

iii. Experiments were conducted with regard to the effect produced on the ionic mobilities in air by adding small quantities of vapours. The mobilities showed a marked

decrease on the addition of alcohol and acetone, but were not sensibly affected by the addition of the heavier vapours of methyl iodide and ethyl bromide.

iv. Experiments were performed with regard to the ionic mobilities in mixtures of a gas and a vapour, the ions being formed from the latter constituent only. As a result of the experiments, it was shown that there must be, at all events initially, a transference of the charge (both positive and negative) from the vapour to the gas molecule.

v. Experiments were performed with regard to the stability of the vapour ions in the presence of hydrogen; it was shown that the vapour molecules can accompany the charge to an appreciable extent, even in the presence of a considerable quantity of hydrogen.

vi. The mechanism by which the transference of charge from one molecule to another is effected has been discussed; there is reason to believe that the transference takes place by the medium of a detachable unit of positive electricity.

vii. From the experimental results a theory of the mechanism underlying the passage of electricity through gases at ordinary temperatures and pressures has been deduced.

"A Study of the Use of Photographic Plates for the Recording of Position." By Dr. C. E. K. MEES.

"The Coefficients of Capacity and the Mutual Attractions or Repulsions of Two Electrified Spherical Conductors when close together." By ALEXANDER RUSSELL, M.A., D.Sc., M.I.E.E.

"On the Effect of Previous Magnetic History of Magnetisation." By ERNEST WILSON, G. E. O'DELL, and H. W. K. JENNINGS.

FARADAY SOCIETY.

Ordinary Meeting, June 15th, 1909.

Dr. N. T. M. WILSMORE in the Chair.

MR. E. R. TAYLOR, Chairman of the Conservation Committee of the American Electro-chemical Society, delivered an Address, which was profusely illustrated with lantern-slides, on *"The National and International Conservation of Water for Power."*

The author began by pointing out that the water-power capacity of the United States with proper conservation is not less than 150 million H.P., without considering the storage capacity of brooks. The annual stream-flow in the same country is 70 million million cubic feet, of which less than 1 per cent is restrained and utilised for municipal supply and such purposes, less than 2 per cent is used for irrigation, 5 per cent for navigation, and less than 5 per cent for the production of power. From 85 to 95 per cent is wasted in floods. This illustrates the kind of waste that is going on all over the world, and typical examples of such wasted resources were described and illustrated by the author, who strongly advocates the impounding of flood-waters in the uplands with its accompanying afforestation of the hills, and the simultaneous conservation of sources of power, which are vast in the aggregate, and which at present are almost entirely uncontrolled and untapped. Many instances were given of the advantages that had accrued from the proper utilisation of this waste water, both on small farms from the impounding of a mere brook, to the damming of great rivers and the consequent enrichment of vast tracts of country. The electro-chemical industries in particular would benefit by the creation of cheap and abundant sources of power, on which their very existence depends. The lecturer strongly urged the necessity for this problem being considered internationally by all the civilised peoples of the world. A beginning will be made in 1910, when an international conference will be held at the Hague.

Mr. WALTER REID pointed out that the conservation of water-power over large areas might be very difficult of

accomplishment in England, where the value of land was so high, and where there was a large number of cities very close together. Moreover, the question of scenery, which was a national possession, had frequently to be taken into consideration. The Government had, however, recently promised, through the President of the Local Government Board, to take action with regard to the conservation of all British rivers, each of which was to be placed under the control of one central authority.

Mr. W. MURRAY MORRISON showed how nothing but good had followed the development of the power schemes at Foyers and Loch Leven, now the centres of a flourishing industry and population. There were many such possible centres of power, especially in Scotland. Water-power was one of the most formidable weapons with which a nation had to fight the modern war of industry.

Dr. H. BORNES emphasised the importance of bringing home to the nation the value of the small water-power.

The CHAIRMAN remarked on the way in which the land was entirely utilised in Germany, where 20 per cent of the land was forest, and no part, as far as he knew, was given over to waste.

Mr. W. FIELDING contributed a paper entitled *"The Formation of Silicon Sulphide in the Desulphurisation of Iron."*

In the refining of steel in the electric furnace a very complete desulphurisation of the metal can be effected, and this action is facilitated by the addition of a charge of ferrosilicon. Several explanations have been put forward to account for this influence on the removal of sulphur.

The object of the author was to investigate the conditions under which ferrosilicon can react with ferrous sulphide, and liberate a sulphide of silicon, and the reaction of the two compounds was investigated by heating intimate mixtures of them in a vacuum at known temperatures. The heating was effected in a crucible in the form of a hollow graphite rod, heated electrically.

When the commercial variety of iron sulphide was used the mass fused at a temperature of about 930° C., and a vigorous reaction set in with rise of temperature. Using pure iron sulphide (free from oxide) no reaction was observed up to about 1300° C., hence the reaction noted in the first case was probably due to reduction of oxide of iron present by the ferrosilicon. This explains the sudden rise of temperature noted.

In all the experiments a yellow sublimate began to appear on the walls of the tube at a temperature of 1500° C. A larger quantity of this product was subsequently prepared, and found to consist of approximately 50 per cent silicon sulphide (assuming the formula to be SiS₂), the remainder being iron sulphide which had volatilised, silica (obtained from the action of moisture in the air on the silicon sulphide), and a small amount of ferric oxide in a finely divided state. In different experiments products of variable composition were obtained, and it has not been possible to fix the identity of the sulphide of silicon present in the product.

Prof. A. K. HUNTINGTON (communicated) thought it more probable that what was sublimed was a silico-sulphide of iron. He believed that oxysulphides of metals were formed more often than is generally supposed.

Mr. F. E. POLLARD (communicated) controverted the author's assumption that the sulphur exists in combination with the iron. He considered that sulphur exists almost entirely in combination with the manganese.

The CHAIRMAN said that silicon sulphide was not the indefinite substance the author imagined; three compounds—SiS₂ (white), SiS (yellow), and SiOs—had been isolated.

"A Contribution to the Study of Electric Furnaces as Applied to the Manufacture of Iron and Steel" was communicated by CHARLES A. KELLER.

The author prefaces his paper with the opinion that the electrical production of steel in electrode furnaces necessitates their being fitted with hearths of a conducting

material that will not carbonise the metal produced. Conducting hearths at present in use are mostly made of a layer of agglomerate carbon or of a bundle of electrodes. The upper electrode, being kept in the slag, will not operate as a carbonising agent.

The author proceeds to describe the various classes of conducting hearths, classifying them as follows:—

(a) Those made entirely of metal, water-cooled. These have no industrial value.

(b) Those consisting of one or more metallic poles (or graphite protected by metal) embedded in a non-carbonising masonry. The original furnace of Siemens and furnaces by Borchers and Girod are of this type. Various forms of the latter are described.

(c) Those consisting of a hearth of refractory material, such as magnesite or silica, rendered conducting by a carboniferous substance. The Firminy furnace, of which at present only a small example has been constructed, is of this type.

(d) Furnaces with a hearth made up of a mixed conducting material; this is the type devised by the author. The hearth consists of "reinforced clay," made up of iron bars 25 to 30 mm. in diameter, placed vertically 25 to 30 mm. apart, and packed solid with magnesite, by preference. When cold, of course only the bars are conducting, but when in operation the hearth is conductive over its whole section, and the electrical resistance is very small. The mechanical resistance of such a hearth to the subsidence of the metallic bath is very considerable, and the author states that the bottom of the furnace is absolutely indeformable. The hearth of a 1500 kg. furnace, examined after many months' service, was in exactly the same condition as when it started.

The author has made a comparative study of the more usual type of furnace, with vertical electrodes in series, serving as entrance and exit for the current, and the furnace with conducting hearth, and he concludes that the latter has metallurgical advantages over the former for furnaces of moderate size, since the current traverses the whole mass of metal, and thus renders it more homogeneous. Moreover, the furnace is very simple mechanically. On the other hand, the series electrode furnace is of simpler construction, and only half the current density is necessary for the same output, thus economising electrical connections. The furnace with conducting hearth will need careful design to minimise the self-induction and increase the power factor, and a low frequency, say, about 20, should be employed. With this frequency, a power-factor of 0.9 should be attained with a 1000 kw. furnace.

The remainder of the paper describes in detail the construction and performance of the various furnaces the author has erected. These furnaces are furnished with vertical electrodes both for the entry and exit of the current, and they are characterised by the separate regulation of the two fires created by each electrode. The most important example is the 8 to 10 ton furnace in operation at the Holtzer Steel Works at Unieux. This is in reality two superimposed electric furnaces, of which the upper is used for melting and oxidising the billets of iron and steel, and the second for purifying the molten steel. The Holtzer furnace has four movable electrodes, each pole consisting of two electrodes, which can be regulated so as to alter the voltage or current by displacing either or both pairs. This method of central distribution of current results in very small self-induction; the power-factor is 0.97 when 12,000 ampères are passing. A detailed account is given of the performances of this furnace, which can purify the steel until the phosphorus and sulphur together only total 0.01 per cent. This is claimed to be a new metallurgy, not as regards the materials obtained, but as regards the methods employed. A brief consideration of a three-phase furnace, with electrodes connected either in mesh or star, concludes the paper. The author is of opinion that a 20-ton three-phase furnace, of about 1800 kw., could now be constructed. Such a furnace could purify 250 to 300 tons of steel per day, obtained from

a Thomas converter, at an operating cost of 15 to 20 francs per ton, with electricity at 0.15d. a unit, such as would be obtainable by utilising blast-furnace gas.

Mr. J. HARDEN considered a water-cooled electrode beneath a furnace hearth far too dangerous an arrangement to be generally adopted. He thought electrode furnaces would be of limited application on account of the difficulty of procuring electrodes. The variations of power, 30 to 35 per cent, in these furnaces were very great.

Mr. E. RISTORI, Mr. COBB, and Mr. W. MURRAY MORRISON all agreed with the last speaker in his criticism of the water-cooled bottom electrode. The latter, however, did not consider there was any difficulty with regard to procuring electrodes, the consumption of which was comparatively very small.

M. GUSTAVE GIN communicated a paper entitled "*Automatically Circulating Furnaces of the Gin Type for the Electrical Production of Steel.*"

The paper describes induction furnaces in which the molten material is in continual circulation, thus causing a better distribution of heat and of the purifying reactions than in the ordinary induction furnace. The furnaces are composed of two crucibles communicating by inclined channels, the whole arrangement forming a closed circuit in which the heat generated causes a general circulation. Every portion of the molten mass comes rapidly into contact with the oxidising slag, and the very high temperature attained does not introduce the "pinch" effect in the heating channels. It is claimed that with this type of furnace the ohmic resistance of the circuit can be increased with correspondingly altering its self-induction, thus allowing furnaces with a high-power factor to be constructed, and generators and transformers of normal frequency and size to be employed. A 5-ton 420 kw. furnace is illustrated, designed to take current at 4800 volts at a frequency of 5. The author also describes an electrode furnace in which the same system of automatic circulation is applied, by cross-connecting the separate crucibles into which the electrodes dip by means of inclined channels, sloping in opposite directions. Finally, the author describes a combined induction and electrode furnace similarly arranged for automatic circulation of the fluid steel. In this internal heating in the channels, generated inductively, and superficial heating in the two connected crucibles, obtained at the electrodes, are simultaneously made use of. To the paper is added an appendix which gives the calculations necessary for the design of these types of furnaces.

NOTICES OF BOOKS.

The Journal of the Association of Teachers in Technical Institutions. Vol. II., No. 2. London: St. Bride's Press, Ltd. 1909.

In extending the size of this journal the editor has hoped to increase its value to teachers in technical institutions, and to make it something more than the organ of the Association. For this purpose articles of interest written by experts are for the future to form a large part of each issue, and apparently it is proposed that each number should deal more particularly with one branch of technical instruction. This number contains a very practical paper on laboratory work in mechanical engineering, which contains many hints on the fitting up of a laboratory. Machine drawing is also treated, and a syllabus is given of a full course of instruction in chemistry for engineers. In addition the journal contains the reports from different branches of the Association, and reviews of books which have recently appeared, together with some notes on current topics which are of interest to teachers in technical schools.

The Interpretation of Radium. By FREDERICK SODDY, M.A. London: John Murray. 1909.

The author's knowledge of his subject, no less than his attitude of toleration towards views he does not share,

point him out as well fitted to produce that kind of book the production of which offers opportunity for the display of ingenuity and resource—the treatise on a scientific subject for the general reader, in which only non-technical phraseology shall be employed. Nobody who opens this book can fail to feel its fascination, and many students of science will by reading it be enlightened as to the far-reaching importance of the science of radio-activity, which the author believes to be a subject soon to be included in every school curriculum. With the enthusiasm and insight of a master, many of whose prophecies have been verified, he regards the phenomena of radio-activity as providing a key for some of the many riddles which so far science has had to leave unanswered; for instance, to take a simple example, it points out a way of reconciling the age of the earth according to the geologist with the period given by the physicist. Every word of the author's carries weight, and the book worthily expounds a subject enjoying the unique position of the science which may be regarded as the most important outcome of the researches of the 20th century.

Physikalische Chemie der Metalle. ("Physical Chemistry of the Metals"). By Dr. phil. RUDOLF SCHENCK. Halle-a.-S.: Wilhelm Knapp. 1909.

THIS book treats of the scientific foundations of metallurgy, and although the six lectures it contains were intended more particularly for engineers, they are by no means without value for other classes of readers. Many students who are beginning a course of physical chemistry will find that one of the easiest ways of getting a really good grasp of the theory is to study examples of its practical applications, and the investigation of, for instance, the nature of alloys by physico-chemical methods, if carefully followed, will make both the methods of reasoning and the conclusions very clear. The properties and changes of state of the metals are well treated, as is also the application of the laws of chemical equilibrium to the study of the metallurgical processes of oxidation and reduction.

Practical Organic Chemistry. By J. J. SUDBOROUGH, Ph.D., D.Sc., F.I.C., and T. CAMPBELL JAMES, M.A., B.Sc. London, Glasgow, Dublin, Bombay: Blackie and Son, Ltd. 1909.

A COMPLETE course of practical work in organic chemistry to be used in connection with Sudborough's edition of Berthsen's "Organic Chemistry" is given in this book. The order in which the compounds are taken up agrees with that adopted by Berthsen, and the general plan of the book is very much the same. Methods of preparing typical compounds are described with full experimental details, as well as a certain amount of analytical work. The latter includes ordinary combustions and elementary analysis, and also the identification of various classes of compounds by chemical means. The application of physical methods to the investigation of organic derivatives is not neglected, and directions are given for the manipulation of polarimeters, &c. A feature to be specially noticed is the attention paid to modern adaptations of apparatus. References are frequently given to original papers and photographs and diagrams of apparatus, which show the details very plainly, are included.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlviii., No. 20, May 17, 1909.

Viscosity of Solutions of Bases.—D. E. Tsakalotos.—The determination of the viscosity of solutions of triethylamine, pyridine, piperidine, and nicotine shows that these bases form molecular compounds with water, i.e., they exist in aqueous solution in the form of aquo bases.

This appears to confirm Werner's modification of Arrhenius' theory, that inorganic bases combine with water, giving as cations (metal-water)⁺ and (OH)⁻, while the organic bases give as cations (base-hydrogen)⁺, and the anion is again (OH)⁻. From this theory the different properties of aqueous solutions of organic bases (solubility, viscosity, density, thermic effects, &c.) can be foretold.

Study of the System Water-Liquid Ammonia.—E. Baud and L. Gay.—The authors have measured the quantities of heat disengaged and the contractions which occur when water and anhydrous liquid ammonia are mixed. From the results of their experiments they conclude that in aqueous solutions of ammonia the hydrate NH₃.H₂O exists in equilibrium with water and free ammonia.

Colouring Power of Lead Chromate.—Léo Vignon.—Precipitated lead chromate dyes silk, wool, and cotton equally well, differing from the soluble dyes orange II., picric acid, and rocelline as regards the conditions of fixation. To obtain a given shade much more lead chromate than soluble dye is necessary. Lead chromate is not fixed chemically by textiles, but its fixation is evidently due to molecular attraction.

Magnesium Derivative of Bipropargyl Octadienedioic Acid.—MM. Lespiau and Vavon.—Bipropargyl yields a hexaiodide, Cl₂=CI—CH₂—CH₂—CI=Cl₂. A magnesium compound can also readily be prepared, and from it the new acid CO₂H—C≡C—CH₂—CH₂—C≡C—CO₂H. This is totally transformed into suberic acid on hydrogenation.

MISCELLANEOUS.

Electrolytic Disinfection.—Our attention has been drawn to a system of disinfection and bleaching which has decided advantages over older methods. By the electrolysis of sodium chloride in an improved apparatus brought out by E. Grether and Co., Manchester, a solution of sodium hypochlorite is produced, containing from 3 to 20 grms. of available chlorine per litre. For laundry work the liquor as run from the electrolyser is diluted considerably with water. It has no caustic or corrosive action on fibres or metals, can be discharged freely into rivers, while if imperfectly washed after bleaching the fabrics are not tendered, rotted, or yellowed. In the electrolyser no chlorine is evolved into the air, and instead of costly platinum electrodes, carbons are used which have a life of from twelve to eighteen months and cost very little. As a germicide the sodium hypochlorite is most efficacious, and at Poplar Dr. Alexander, the Medical Officer of Health, has used the apparatus for more than a year, and speaks very favourably of the power of the electrolytic liquor in destroying disease germs. In fact the Health Department now is doing more efficiently for £33 what formerly cost about ten times that sum to do.

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THE CHEMICAL NEWS.

VOL C., No. 2589.

A SIMPLE METHOD FOR DETERMINING VAPOUR-DENSITIES AND FOR ANALYSING BINARY MIXTURES.*

By PHILIP BLACKMAN.

Apparatus.

THE apparatus consists of a cylindrical vessel, closed at one end, and having at the other end a conical neck (the narrower end outwards) with a perfectly fitting, hollow, ground-glass stopper (see Fig. 1). The number repre-

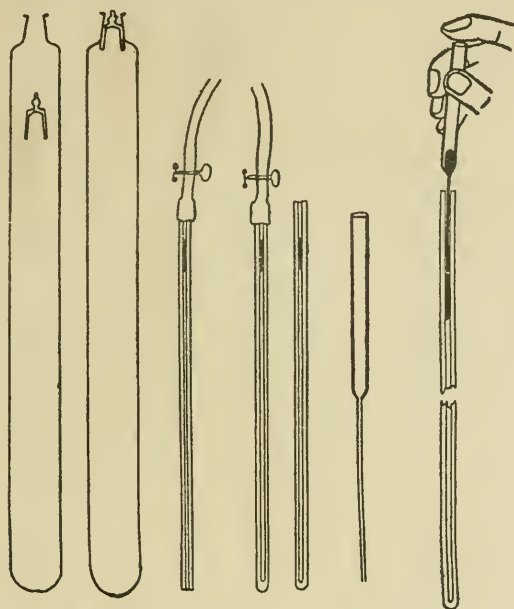


Fig. 1. Fig. 2. Fig. 3. Fig. 4. Fig. 5.

senting the internal volume (cc.) of the bulb, when the stopper is fixed in the neck, is marked in permanent figures on the glass. (The apparatus is supplied by Messrs. F. E. Becker and Co., Ltd., 17-27, Hatton Wall, E.C.).

Manometer, or Pressure-gauge.

The manometer consists of a glass capillary-tube, somewhat shorter than the length of the body of the vessel, closed at one end and having a mercury-thread in the bore near the other end. It may be made by one of the three following methods, of which the second is perhaps the easiest as regards manipulation:—

1. One end of a piece of capillary-tubing, of the proper length, is sealed off in a flame. The tube is warmed in a flame, and the open end placed in some clean dry mercury; as the glass cools, the air within contracts and a thread of mercury is drawn in.
2. A piece of rubber tubing is fixed on to one end of the capillary-tube, and a thread of mercury sucked up through the other end; the mercury is drawn in

until it reaches a short distance from the rubber-fixed end, and the rubber tube is then closed by means of a clip or pinchcock (see Fig. 2). The other exposed end is now sealed off in the blowpipe flame (see Fig. 3), the clip or pinchcock is removed, and the rubber tube taken off.

3. If the bore of the capillary-tube is not too narrow, one end is sealed off in the blowpipe flame. A refill (see Fig. 4) is made by softening in the flame one end of a piece of glass tubing and drawing it off to a long, fine capillary end. A little mercury is sucked up into it and kept within by placing the forefinger over the wide end; the narrow end is then inserted in the bore of the capillary tube, and when it has reached the desired position there, the hold of the finger is slightly eased, which will allow a thread of mercury to run into that part of the bore (see Fig. 5).

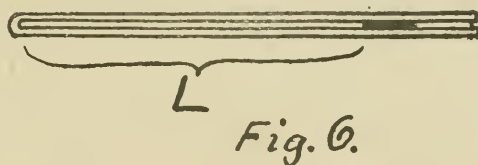


Fig. 6.

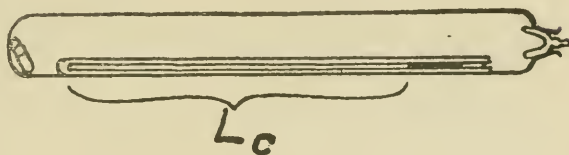


Fig. 7.

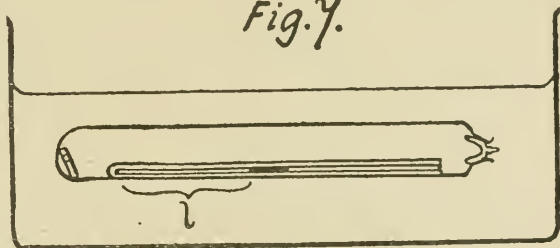


Fig. 8.

Method.

1. The manometer must be allowed to cool to room temperature, placed in a horizontal position, and the length, L , measured in mm., of the enclosed air-thread determined by means of a mm. scale or measure (see Fig. 6).
2. The substance to be experimented on is weighed out (weight = w) in a small stoppered glass weighing bottle.
3. A piece of thread or wire is wound round the handle of the stopper, which is then lowered into the vessel; the manometer and weighing bottle are placed within it, and the stopper is drawn into the neck and kept in place by winding the same thread or wire round the neck. Keeping the apparatus in a horizontal position, the length, L , in mm. of the manometric air-thread is again measured (see Fig. 7).
4. The external temperature, t_1 , and atmospheric pressure, p , in mm. are determined.
5. The vessel is heated in a horizontal position, in a suitable heating-jacket in the vapour of some substance boiling at a temperature above that at which the substance experimented on vaporises at ordinary atmospheric pressures, or better in a thermostatic trough containing some convenient heating medium such as glycerin or paraffin

* Compare CHEMICAL NEWS, 1907, xcvi., 223; 1908, xcvi., 27, 102; 1909, xcix., 87, 133; Zeit. Phys. Chem., 1908, lxi., 48, 381, 635; 1909, lxx., 549, 745; Journ. Phys. Chem., 1908, xii., 661; 1909, xiii., 138; Les Nouveautés Chimiques pour 1908, 15.

wax. When the substance has completely vaporised and the mercury index within the manometer has become stationary, the length, l , in mm. of the manometric air-thread is measured by means of callipers, compasses, or dividers, the distance between whose feet is then measured off along a mm. scale (see Fig. 8).

6. The vessel is removed, cooled, and opened by tapping the stopper; if the latter is tightly fixed the vessel must be further cooled by means of a little ether, which will have the effect of diminishing comparatively the internal pressure, and then, on tapping, the stopper will be forced inwards. (It is as well to wind loosely round the handle of the stopper and the neck a piece of thread to prevent the stopper flying inwards with violence and consequent risk of damage to the apparatus). The manometer and weighing bottle (opened) are removed and dropped into a burette nearly filled with water; the increase in volume due to their introduction will give the combined volume of the manometer and weighing bottle; the difference in value between this volume and that marked on the body of the vessel represents V , cc., the volume occupied by both the heated air and the vaporised substance.

N.B.—*a.* The need of the thread or wire round the stopper and neck has already been explained. Otherwise the heated gases within exert sufficient pressure to keep the stopper in position, the greater the internal pressure the closer the fit.

b. Before using the apparatus it must be well cleaned and thoroughly dried, and a current of air drawn or blown through it to remove any vapours.

c. It will be found that with this apparatus L and L_c are generally equal in value.

d. The temperature to which the vessel is heated is not required to be known unless for special purposes, such as, for instance, for the calculation of internal pressures (see the end of the paper).

Vapour-densities.

If the vapour-density be d its value is to be calculated from the formula—

$$d = \frac{31068 w l L_c (273 + t_1)}{\rho L V (L_c - l)}$$

Binary Mixtures.

The experiment is carried out as already shown. If the required percentage weights of the two constituents be w and $100 - w_1$, the respective vapour-densities (supposed known) being d_1, d_2 , the calculations are effected by means of the formula—

$$d_2 w_1 + d_1 (100 - w_1) = \frac{100 d_1 d_2 \rho L V (L_c - l)}{31068 w l L_c (273 + t_1)}$$

This formula may also be employed in determining the extent to which a substance, easily decomposed into two components when brought into the gaseous condition on heating, dissociates into its binary constituents.

The apparatus may also be employed to determine the amount, q , of a volatile component, of vapour-density, d , assumed known, given off on heating a compound to varying temperatures (*e.g.*, to measure the quantity of water-vapour evolved from $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), the necessary calculation being carried out by aid of the formula—

$$q = \frac{d \rho L V (L_c - l)}{31068 l L_c (273 + t_1)}$$

Internal Pressures.

The internal pressure (in atmospheres) π , corresponding to the given readings as found, is given by the formula $\pi = \rho L (273 + t_2) / 760 l (273 + t_1)$, t_2 being the temperature to which the vessel is heated.

Hackney Technical Institute,
London, N.E.

THE FORMATION OF SILICON SULPHIDE IN THE DESULPHURISATION OF IRON.*

By W. FIELDING, B.Sc.

THE object of the work was to investigate the conditions under which ferrosilicon can react with ferrous sulphide and liberate a sulphide of silicon.

In the refining of steel in the electric furnace a very complete desulphurisation of the metal can be effected. This action is, in practice, found to be considerably facilitated by the addition of a charge of ferrosilicon.

Several explanations have been put forward to account for this influence on the removal of sulphur. Some have ascribed it to the high temperature produced during the reduction of the ferrous oxide present by the ferrosilicon. Prof. Osann (*Stahl und Eisen*, July 15, 1908) believes that this removal of the iron oxide prevents the back action between it and calcium sulphide; at the same time a higher temperature is produced by the deoxidation, which assists the removal of sulphur as calcium sulphide. At the end of his paper he suggests the possibility of the formation of a gaseous compound, silicon sulphide.

Max Haft (*Electrochem. and Metall. Ind.*, March, 1908, p. 96) had previously declared that silicon sulphide was produced by heating together sulphides and silicides at a high temperature, but no details were given of his experiments. Silicon sulphide (SiS_2) is described (Hempel and v. Haasy) as a solid at ordinary temperatures, which at a red heat sublimes under 60 mm. pressure.

In the present work the reaction between ferrosilicon and ferrous sulphide was investigated by heating intimate mixtures of these compounds in a vacuum at known temperatures. The reacting substances were placed in a crucible in the form of a hollow graphite rod, which could be evenly heated by the passage of an electric current. Electrical connection was made with the rod by fitting it in graphite plugs, which in turn were soldered into water-cooled brass tubes to which cables could be attached (compare Pring and Hutton, *Trans. Chem. Soc.*, 1906, lxxix., 1593; and H. C. Greenwood, *Trans. Chem. Soc.*, 1908, xciii., 1485). The rod was surrounded by a water-jacketed Jena glass tube, for experiments in which the rod was heated below 1500° ; above this temperature a silica tube was employed. The apparatus was made air-tight by luting the ends of the tube with soft wax. Temperature readings were made by means of the Wanner optical pyrometer in those cases in which a glass tube was employed, and changes in pressures were indicated by a mercury gauge connected with the tube (see Fig.).

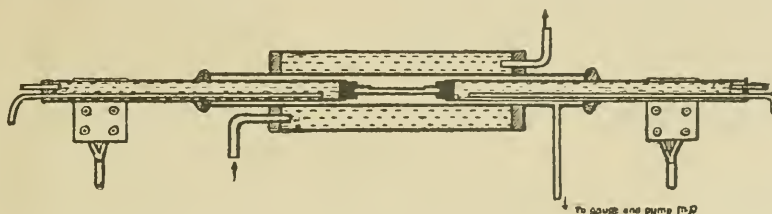
In experiments in which the commercial variety of iron sulphide was used the mass fused at a temperature of about 930°C. , and a vigorous reaction set in with rise of temperature. In later experiments, using pure iron sulphide (free from oxide), no reaction was observed to about 1300°C. , hence the reaction noted in the first case was probably due to reduction of oxide of iron present in the iron sulphide by the ferrosilicon. This explains the sudden rise of temperature noted.

In all the experiments a yellow sublimate began to appear on the walls of the tube at a temperature of 1500°C. On removing this product and treating with water a rapid effervescence took place, sulphuretted hydrogen being liberated and silica separating. A larger quantity of this product was prepared by placing a mixture (40 grms.) of ferrosilicon and ferrous sulphide in a long graphite tube, which was closed at one end and fitted at the other into a porcelain tube to serve as condenser. The graphite tube was then placed in a horizontal carbon tube furnace with the porcelain tube projecting outside, and the temperature was raised in stages. No sublimate was formed until a temperature of 1700°C. was reached (the higher temperature required in this case being probably due to the experiment being carried out at atmos-

* Read before the Faraday Society, June 15, 1909.

pheric pressure instead of at reduced pressure as before), when a yellow vapour was evolved, which condensed partly in the tube, the remainder being carried along by the stream of carbon monoxide gas coming off, which on being burned at the end of the tube smelled strongly of sulphur dioxide. About 4 grms. of the product were obtained, which on analysis was found to consist of approximately 50 per cent silicon sulphide (assuming the formula to be SiS_2), the remainder being iron sulphide which had volatilised, silica (obtained from the action of moisture in the air on the silicon sulphide), and a small amount of ferric oxide in a finely divided state. In different experiments products of variable composition were obtained.

The silicon sulphide was estimated by acting on it with water in a Schrotter's apparatus (fitted with a calcium chloride drying tube) and determining the weight of sulphuretted hydrogen evolved. The gas evolved, after being efficiently dried by calcium chloride, was passed into weighed potash bulbs, and the increase in weight of the potash bulbs was found to correspond to the loss in weight of the Schrotter's apparatus. The weight of silicon sulphide (SiS_2) corresponding to this weight of sulphuretted hydrogen was then calculated. The product remaining



in the apparatus was then treated with dilute sulphuric acid, and the gas evolved driven over into weighed potash bulbs, and the corresponding amount of ferrous sulphide was further confirmed by determining the amount of iron present in the solution, which was found to correspond to the amount of iron sulphide present.

It will be observed that it has not been possible to fix the identity of the sulphide of silicon present in the product. An attempt was made to prepare the silicon sulphide in greater purity by distilling the product *in vacuo*, but up to 1100°C . no volatilisation was observed. No attempt was made at higher temperature, as iron sulphide is also volatile above 1100° . According to Hempel and v. Haasy silicon sulphide (SiS_2) distils at red heat under 60 mm. pressure; this tends towards the conclusion that it is a much less volatile sulphide of silicon which is here produced.

Rubidium Peroxide Hydrate and Rubidium Percarbonate.—Erich Peltner.—The action of hydrogen peroxide solution on solutions of rubidium hydroxide in absolute alcohol gives a strongly hygroscopic and unstable compound, the analysis of which presents many difficulties. If, however, it is protected from the action of damp air a rapid analysis can be performed. The results of such experiments showed that its composition is expressed by the formula $\text{RbOOH} \cdot \text{H}_2\text{O}_2$. The substance when first prepared is white, but it rapidly turns yellow, and apparently the compound $\text{RbOOH} \cdot \text{H}_2\text{O}_2$ is transformed into the higher oxide Rb_2O_4 with loss of water. Percarbonates of rubidium, $\text{Rb}_2\text{CO}_4 + 2\text{H}_2\text{O}_2 + \text{H}_2\text{O}$, $\text{Rb}_2\text{CO}_4 + \text{H}_2\text{O}_2 + 2\text{H}_2\text{O}$ and $\text{Rb}_2\text{CO}_4 + 2\frac{1}{2}\text{H}_2\text{O}$, can be prepared by leading CO_2 into the peroxide hydrate. These are very hygroscopic substances which readily lose active oxygen. This research shows that rubidium, unlike sodium and potassium, is capable of yielding higher compounds with H_2O_2 . This was to be expected, for the peroxide of rubidium, Rb_2O_4 , contains considerably more active oxygen than the peroxide of sodium Na_2O_2 .—*Berichte*, xlii., No. 8.

THE VOLUMETRIC ESTIMATION OF POTASSIUM IN ANIMAL FLUIDS.

By W. A. DRUSHEL.

THE distribution of potassium in plant and animal tissues has been studied by Macallum (*Journ. of Physiol.*, xxxii., 95) and others. Macallum precipitated potassium in place as potassium sodium cobalti-nitrite, an insoluble potassium salt which by its crystalline form and colour is easily recognisable under the microscope. To study the function of potassium in the animal organism it is desirable to have a simple and rapid method for its estimation in the various tissues and fluids. A number of quantitative methods have been proposed which, however, are not wholly free from objections.

M. Kretschy in 1876, after having carefully studied the several indirect methods for potassium and sodium in the presence of each other, finally adopted a modification of the chlorplatinate method for potassium in the presence of relatively large amounts of sodium in physiological work. He worked with quantities of potassium ranging from 3 mgrms. to 120 mgrms., precipitating it as the chlor-

platinate in the usual manner. The washed and dried precipitate was carefully ignited, the residue extracted with water, and the extract evaporated to dryness. This residue was gently ignited and weighed as potassium chloride. A small amount of platinum usually passed through the filter, giving a result which was too high for potassium chloride. To avoid error on this account the weighed potassium chloride was dissolved in water, any residue of platinum filtered off on ashless paper, ignited, and weighed, and the necessary correction made in the weight of the potassium chloride.

Some years later Lehmann (*Zeit. Physiol. Chem.*, viii., 508), Bunge (*Zeit. Biologie*, ix., 139), Heintz (*Pogg. Ann.*, lxi., 133), and Pribram and Gregor (*Zeit. Anal. Chem.*, xxxviii., 409) used different modifications of the Fresenius chlorplatinate method for the estimation of potassium in urine. In the methods of Lehmann, Bunge, and Pribram and Gregor the sulphate radical was removed by an excess of barium hydroxide or barium chloride; subsequently the excess of barium was removed by ammonium carbonate and ammonium hydroxide, or in case of barium hydroxide by carbon dioxide. Lehmann evaporated the urine with ammonium sulphate before ashing the residue, while Bunge treated the urine directly with barium hydroxide. Pribram and Gregor oxidised the organic matter by heating the urine, acidified with sulphuric acid, to the boiling-point and adding an excess of potassium free barium permanganate. Heintz treated 20 cc. to 30 cc. of clear urine with chlorplatinic acid and a threefold volume of a 1:4 ether and absolute alcohol mixture. After standing twenty-four hours the precipitate was filtered off, washed with alcohol, dried, ignited, and weighed. The residue was then extracted with hot water, and again dried and weighed. The amount of potassium chloride was found by taking the difference of the weights. It has been repeatedly shown that appreciable amounts of the alkali salts are carried down by barium sulphate, which cannot be completely removed by washing. This objection applies to all of the methods in which the sulphate radical is removed by means of a barium salt. The loss of alkalis is especially appreciable where a large amount of barium

sulphate is formed in the presence of relatively small amounts of the alkali salts.

In 1898 K. Gilbert devised a method for the separation of potassium which does not require the previous removal of the sulphate radical. He treated a potassium salt solution free from mineral acids with an excess of sodium cobalti-nitrite acidified with acetic acid. After standing from twelve to twenty hours the potassium was quantitatively separated out as potassium sodium cobalti-nitrite which could be freely washed with cold water without an appreciable loss. Gilbert decomposed this precipitate by heating with dilute hydrochloric acid, and estimated the potassium as the perchlorate or chlorplatinate.

A few years later Autenrieth and Bernheim (*Zeit. Physiol. Chem.*, xxxvii., 39) used Gilbert's method for separating potassium in urine, subsequently estimating the potassium as the perchlorate. They used 6 cc. to 10 cc. of concentrated sodium cobalti-nitrite to precipitate the potassium in 50 cc. of urine. At this dilution it had been shown by Gilbert that the potassium is quantitatively precipitated, and that the precipitate is apparently of indefinite composition. In 1900, however, Adie and Wood found that with a sufficiently high concentration of the reagent and of the potassium salt solution a precipitate of definite composition, represented by the formula $K_2NaCo(NO_2)_6 \cdot 6H_2O$, is obtained (*Journ. Chem. Soc.*, lxxvii., 1076). They further found that by decomposing this precipitate with boiling dilute sodium hydroxide and titrating the nitrites with standard potassium permanganate the potassium may be estimated with a fair degree of accuracy.

In a previous paper (*Am. Journ. Sci.*, 1907, xxiv., 433) from the Kent Chemical Laboratory of Yale University, it was shown that it is unnecessary, after adding the cobalti-nitrite reagent, to let the mixture stand from twelve to twenty hours, if it is evaporated nearly to dryness, also that the precipitate may be directly oxidised with potassium permanganate without previously decomposing it with boiling sodium hydroxide. Later, it was found that a half saturated sodium chloride solution is preferable to cold water for washing the precipitate, since it permits the use of a coarser asbestos felt in filtering without danger of loss.

The method used in the work on animal fluids is as follows:—A potassium salt solution was obtained free from mineral acids and ammonia salts, and treated with a liberal excess of concentrated sodium cobalti-nitrite in an evaporating dish. The mixture was evaporated to a pasty condition over the steam-bath. After cooling the residue it was stirred up with enough cold water to dissolve the excess of sodium cobalti-nitrite. The precipitate was permitted to settle a few minutes, then it was filtered on asbestos in a perforated crucible, and washed with the sodium chloride solution until the filtrate came through colourless. The precipitate and felt were transferred by means of a spray of water and a stirring rod to a beaker containing a measured amount (being an excess) of standard decinormal or fifth normal potassium permanganate, diluted about ten times, and heated nearly to boiling. The permanganate solution was kept hot, and stirred to facilitate the solution and oxidation of the precipitate, the oxidation being completed by adding 5 cc. to 10 cc. of dilute sulphuric acid, and stirring for a minute or two. The excess of permanganate was then bleached by a measured amount of standard decinormal oxalic acid, and the solution titrated to colour with standard permanganate. In this process the cobalt is reduced to the bivalent condition and the nitrites oxidised to nitrates, from which by a simple calculation it is found that 1 cc. of strictly decinormal permanganate is equivalent to 0.000857 grm. of K_2O .

The modified Lindo-Gladding method was used as a control in the experimental work of this paper. The potassium was obtained as the sulphate in the presence of sodium sulphate, and possibly traces of calcium and magnesium sulphate. The solution of these sulphates was treated with an excess of chlorplatonic acid, evaporated nearly to

dryness, and the precipitate washed free from the excess of chlorplatonic acid with 85 per cent alcohol. The precipitate was then washed three or four times with a 20 per cent solution of ammonium chloride saturated with potassium chlorplatinate, and finally again two or three times with 85 per cent alcohol. By this treatment the sodium sulphate and the small amounts of calcium sulphate and magnesium sulphate are completely removed.

A. Potassium in Urine.

The following table gives approximately the amount of the constituents present in a day's excretion of urine of an adult in normal health and on an ordinary mixed diet:—

	Grms.
K_2O	2 to 4 (a)
$NaCl$	10 to 15
CaO and MgO	0.8
NH_3	0.7
P_2O_5 (phosphates)	1.5
H_2SO_4 (sulphates)	2.5
Urea	30
Uric acid	0.7
Creatinine	1.5
Hippuric acid	0.7
Other organic bodies	2.1

(a) Taken from Hammerstein's "Physiological Chemistry" (Mandel's Translation), 5th Ed., p. 628.

In this list of constituents ammonia and the organic bodies, especially urea, are the only ones which should interfere with the volumetric method as previously described. To remove these bodies without the loss of potassium is apparently the only new problem.

In the experiments recorded in Table I. aliquot portions of urine of 10 to 50 cc. each were measured with pipettes or a burette into small platinum evaporating dishes, and evaporated to dryness over the steam-bath in a good draught hood. The residues of the aliquots of the first specimen were treated with 5 cc. of concentrated nitric acid, and again evaporated to dryness. These residues were then moistened with concentrated sulphuric acid, and ignited to a white ash, beginning with a low flame and increasing the heat until the organic matter was burned off, and the ammonium sulphate and excess of sulphuric acid completely removed. In subsequent experiments it was found more expeditious to treat the dried urine residue with 5 cc. to 10 cc. of a 9 : 1 nitric-sulphuric acid mixture, in a covered evaporating dish, removing the cover when the first violent oxidation is over, evaporating to dryness, and igniting without the further addition of sulphuric acid. By this treatment the ignition of the residue from 50 cc. of urine could be readily made in thirty minutes without loss of material. The residue thus prepared was treated with a little water and a few drops of acetic acid to dissolve the alkalis. Without filtering, about 10 cc. of concentrated sodium cobalti-nitrite were added, and the mixture evaporated to a pasty condition. From this point the process was carried out as previously described. In the control experiments the phosphoric acid was removed by a slight excess of calcium hydroxide, and the calcium by ammonium oxalate, before the ignition of the residue.

The results obtained by the two methods from a number of different specimens of human urine are given in Table I.

B. Potassium in Circulatory Fluids.

An additional difficulty presents itself here in the presence of a large amount of protein material which cannot be removed by coagulation and filtration without a considerable loss of potassium. This is particularly true of the blood, where most of the potassium is intimately associated with the protein of the corpuscles. It is necessary therefore to decompose the protein material by oxidation.

The nitric-sulphuric acid mixture was first used for oxidising the dried blood residue, but was found to work less satisfactorily than in the case of urine. In the

TABLE I. (A).

Urine taken. Cc.	Sp. gr.	K found. Grm.	K found. Per cent.	Method.
I.				
1.	10	1'018	0'0124	Vol.
2.	10	—	0'0122	"
3.	10	—	0'0123	Grav.
4.	10	—	0'0131	"
II.				
1.	10	1'022	0'0180	Vol.
2.	10	—	0'0178	"
3.	10	—	0'0178	Grav.
4.	10	—	0'0171	"
III.				
1.	10	1'023	0'0241	Vol.
2.	10	—	0'0242	"
3.	10	—	0'0233	Grav.
4.	10	—	0'0231	"
IV.				
1.	10	0'024	0'0241	Vol.
2.	10	—	0'0243	"
3.	10	—	0'0242	Grav.
4.	10	—	0'0243	"

TABLE I. (B).

Urine taken. Cc.	Sp. gr.	Vol. in 24 hours. Cc.	K in Grm.	K in 24 hours. Grms.	Method.
V.					
1.	10	1'025	950	0'0293	Vol.
2.	10	—	—	0'0292	"
3.	10	—	—	0'0293	Grav.
4.	10	—	—	0'0292	"
VI.					
1.	25	1'025	950	0'0740	Vol.
2.	25	—	—	0'0747	Grav.
3.	25	—	—	0'0740	Vol.
VII.					
1.	20	1'025	910	0'0757	Vol.
2.	20	—	—	0'0752	Grav.
3.	20	—	—	0'0764	Vol.
VIII.					
1.	20	1'024	1130	0'0663	Vol.
2.	20	—	—	0'0662	"
3.	20	—	—	0'0663	Grav.
4.	20	—	—	0'0662	"
IX.					
1.	25	1'018	1500	0'0425	Vol.
2.	50	—	—	0'0839	Grav.
3.	50	—	—	0'0843	Vol.
4.	25	—	—	0'0424	Grav.

ignition of the blood residue oxidised in this way there was apparently a greater tendency to spatter, probably due to the presence of the sulphuric acid. When, however, nitric acid alone was used for the oxidation, there was a tendency for the residue to burn off explosively on ignition. The analytical results from the first specimen in Table II. were obtained by treating weighed portions of defibrinated blood with about 2 cc. of bromine in covered evaporating dishes, allowing them to remain in a warm place under the hood for about one hour. The excess of bromine was then removed over the steam-bath, the residue evaporated to dryness, and ignited sufficiently to char the organic matter. The residue was thoroughly extracted with hot water, and the extract evaporated off with a few drops of sulphuric acid. The residue was then ignited to remove any ammonium salt which might have escaped the action of the bromine and any organic matter which might have passed through the filter.

The second specimen was a half litre of clotted sheep's blood, from which no homogeneous portions could be taken. The whole mass was therefore evaporated over a steam-bath and oxidised with concentrated nitric acid, getting everything into solution except a little lipid material. The solution was made up to the original volume, and aliquots of 25 cc., representing 30 grms. of blood, were pipetted off. These portions were evaporated to dryness and gently ignited, but not sufficiently to produce explosive decomposition. The residues were then moistened with concentrated sulphuric acid, and ignited carefully to remove the organic matter and the ammonium salts. For the results of the second and third divisions of Table II. weighed portions of serum and lymph were similarly oxidised with nitric acid, and subsequently ignited with a little sulphuric acid. The potassium in all the residues thus obtained was estimated gravimetrically or volumetrically as previously described. The results obtained for potassium in circulating fluids are given in Table II.

TABLE II.

Amount taken. Grms.	K ₂ O found. Grm.	K ₂ O found. Per cent.	Method.
I. Defibrinated Pig's Blood.			
1.	10'89	0'0227	Grav.
2.	11'21	0'0228	Vol.
3.	20'33	0'0391	"
4.	10'16	0'0203	"
5.	10'85	0'0211	"
6.	11'03	0'0236	"
II. Sheep's Blood.			
1.	30'00	0'0174	Grav.
2.	30'00	0'0179	Vol.
3.	30'00	0'0181	Grav.
4.	30'00	0'0181	Vol.
5.	30'00	0'0180	"
III. Serum of Dog's Blood.			
1.	10'11	0'0024	Vol.
2.	10'04	0'0024	Grav.
3.	10'07	0'0023	Vol.
IV. Dog's Lymph.			
1.	10'28	0'0018	Grav.
2.	10'01	0'0019	Vol.
3.	10'00	0'0020	"
4.	10'03	0'0019	"
5.	10'12	0'0019	"
6.	10'32	0'0022	Grav.

C. Potassium in Milk.

In addition to lactose and the inorganic salts, milk contains a large amount of protein, chiefly casein, and varying amounts of fat. The ease with which casein is precipitated suggested the possibility of making a complete separation of the inorganic salts and casein, but it was found that after thoroughly washing the precipitated casein it still contained appreciable amounts of potassium. It was found preferable to evaporate weighed portions of milk to dryness, oxidise with concentrated nitric acid, again evaporate to dryness, and ignite gently until most of the organic matter was burnt off, finishing the ignition after moistening the residue with concentrated sulphuric acid. In the residues thus obtained the potassium was estimated gravimetrically or volumetrically as in the previous work.

The results obtained for potassium in two specimens of cow's milk are given in Table III.

Summary.

Where protein does not occur in animal fluids it was found most advantageous to oxidise the dried residue with a 9 : 1 nitric-sulphuric acid mixture. In the presence of protein oxidation by bromine, or by nitric acid alone,

TABLE III.

	Milk taken. Grms.	K ₂ O found. Grm.	K ₂ O found. Per cent.	Method.
I.				
1.	25.8	0.0413	0.16	Vol.
2.	25.8	0.0432	0.17	"
3.	25.8	0.0428	0.17	Grav.
4.	51.6	0.0833	0.16	Vol.
II.				
1.	25.7	0.0454	0.18	"
2.	25.7	0.0457	0.18	"
3.	25.7	0.0451	0.18	Grav.

finishing the ignition in the latter case with a little concentrated sulphuric acid was found more satisfactory.

For the volumetric estimation the ignited residue was treated with a few drops of acetic acid and a little water. To this solution an excess of sodium cobalti-nitrite was added, and the mixture evaporated nearly to dryness. The residue was cooled, treated with cold water, filtered on asbestos, and well washed with a half saturated sodium chloride solution. The precipitate was oxidised by an excess of hot standard potassium permanganate, the solution bleached by an excess of standard oxalic acid, and titrated to colour with permanganate.

For the gravimetric controls the calcium, phosphoric acid, and iron (in the case of the blood) were removed either before or after the oxidation and ignition. The residue of sulphates was dissolved in a little hydrochloric acid and water, and the potassium estimated as the chlorplatinate, taking care to wash the precipitate with alcohol, Gladding's reagent, and again with alcohol.

Conclusions.

The necessity of allowing the cobalti-nitrite mixture to stand from twelve to twenty hours to complete the precipitation, suggested by Gilbert, Adie and Wood, and others, is avoided by evaporating the mixture nearly to dryness. The removal of the cobalt from the precipitate before oxidation with permanganate is unnecessary, since the cobalt is reduced and not re-oxidised in the titration process, and since with proper dilution its colour does not interfere with the end-point.

For small amounts of potassium fairly accurate results are obtained by using the permanganate factor calculated from Adie and Wood's formula for potassium cobalti-nitrite. Sutton has suggested that more accurate results are secured by obtaining a factor empirically from a pure potassium salt. All the results from this and previous papers were obtained, however, by using the theoretical factor calculated from the formula of Adie and Wood, their analyses of potassium sodium cobalti-nitrite having been verified by the analysis of a carefully prepared salt.

The chief sources of error in the method appear to be in the slight solubility of the potassium sodium cobalti-nitrite, being one part in 25,000 to 30,000 parts of water at room temperature, and its tendency to include traces of sodium cobalti-nitrite. These sources of error tend in opposite directions, resulting usually in a positive error, which by proper washing of the precipitate may be kept within fair limits.

The method requires less time and labour than the chlorplatinate method, and is applicable in the presence of substances which form no insoluble cobalti-nitrites, and which neither oxidise oxalic acid nor reduce potassium permanganate.—*American Journal of Science*, xxvi., p. 555.

THE USE OF BAKELITE FOR ELECTRICAL AND ELECTRO-CHEMICAL PURPOSES.*

By L. H. BAEKELAND, Sc.D.

(Continued from p. 7).

The Impregnation of Coils for Dynamos, Motors, and Transformers.—Bakelite gives us a ready means to provide these apparatus with a hard and strong insulating mass which cannot soften under the influence of heat, and withstands temperatures at which all hitherto used gums or resins would melt away. Every electrical engineer knows what this means in relation to running "overloads."

But the use of Bakelite for these purposes involves new questions in the technique of impregnation. It should not be forgotten that by the synthesis of Bakelite, a certain amount of water is set free, and this water must be eliminated from the coils by after drying. Furthermore, Bakelite in its final state C, although very hard and tough, is not flexible; so that any wires or conductors coated with it can no longer stand much bending or twisting, and for such parts the bakelising operation should only take place after all wires and conductors are in their final place.

With this aim in view, the wire or conductor, provided with its covering of cotton or asbestos, can be simply coated with dissolved A solution properly diluted with the necessary amount of alcohol, then submitted to spontaneous drying. This may be helped by a gentle application of heat, but never more than is necessary to carry the material to the stage B, so as to maintain the necessary flexibility. The wire is now wound as usual, and in order to insure more flexibility it may be found useful to heat it slightly. Tape or any fabric, or asbestos impregnated with A, may be put between successive layers, just as is done when shellac is used as an insulator; after the coil is made up it is now introduced in the Bakeliser.

In case the wires are covered exclusively with asbestos it will be advantageous to heat the Bakeliser at highest temperatures; however, if cotton or similar organic materials be present, such high temperatures would destroy and carbonise them, and it may be safer not to exceed 140° C. After bakelising, the coils should be submitted to slow drying so as to expel any remaining traces of moisture or solvents, and this operation can be hastened considerably by the use of a vacuum dryer.

In other cases ready-wound coils may be simply impregnated with liquid A, using the precautions as described for the impregnation of wood. Capillary conditions as described for the wood impregnating process exist here; so that with some precaution it is possible to slowly transform A into C, or at least into B, in an ordinary drying stove, without the absolute necessity of resorting to a Bakeliser; always provided the heating be started at temperatures as low as 60–70° C., and gradually increased to 120–140° C.

In fact it may be found sufficient not to go beyond B, and leave it to future self-heating of the wire when run under overload to arrive at the final condition C.

It ought to be mentioned here that in such coils with many layers of metallic wire, the outer shell of B may act as an envelope which insures internal pressure during the heating process, just as if it was in a closed vessel, and thus prevents dissociation and the resulting formation of a porous mass.

As a modification to above methods, I should suggest the following:—

The coil after being properly impregnated may simply be put in an accurately made closed mould, and the latter may be filled with more A, using pressure if required, so that after bakelising same the whole will come out in accurate size and shape, and present a much neater appearance than the ordinary clumsy coils now in use for dynamo and

* A Paper presented at the Fifteenth General Meeting of the American Electro-chemical Society at Niagara Falls, Canada, May 6th to 8th, 1909.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 5th instant, the Duke of Northumberland, K.G., President, in the Chair. The Duchess of Northumberland, Lady Victoria A. Percy, Mr. H. E. Edmunds, Colonel Sir Charles Euan-Smith, K.C.B., and Mr. Alfred Rowe were elected Members.

motor construction. The very fact that henceforth it is possible to mould coils in regular shapes and most accurate dimensions, may ultimately simplify the construction of this class of machinery and render renewals much easier.

Coating Processes.—The simplest way for coating an object with Bakelite is to dip it in liquid A and then finish it in the Bakeliser. By slightly heating the objects and by using rather thick A, the operation becomes rather simple, especially for metallic objects. Or the A coated objects may be first heated gently in a stove until the A has been transformed in B, and then the object may be transferred to the Bakeliser. Several coats may thus be applied in succession until any desired thickness is attained. This method of building up a thick coat by several layers takes away the danger of cracking or splitting when thick coats are applied all at once.

The sudden contraction during polymerisation has to be taken into consideration here. There is another way of counteracting the effect of too much contraction, namely, the incorporation of suitable filling materials, as silica, or fine sand, clay, slate dust, powdered asbestos, &c. Any of these materials added to liquid A in suitable proportion will give a putty-like mass which can be easily kneaded, specially if slightly heated; it can be applied and modelled to any kind of surface to the desired thickness and shape. This same mass can be rolled out in thin sheets and the latter can be applied on the inside and outside of metallic vessels. The whole can be directly finished in the Bakeliser or be heated previously at low temperatures so as to bring it first in B state. This method gives a ready means for covering iron pipe or pumps or similar objects with a layer of protective material, and thus render them more suitable for chemical engineering purposes. Thick layers of Bakelite without filler, or mixtures containing little filler, do not adhere well to metallic surfaces. But by using more filler, and specially by using gritty materials as fillers, like sand or abrasives, the adherence becomes excellent. For instance, mixtures of emery with about 10 to 15 per cent liquid A can be made so that after Bakelising they will stick to glass to the point that they can no longer be removed unless by chipping off pieces of the glass.

A composite coating of Bakelite can also be applied on wooden or metallic vessels by first dipping a sheet of asbestos in A, partially transform it into B by heating, then stick it, by means of thick A, to the surface which is intended to be protected, and afterwards press it against the surface by means of a hot, smooth plate. The latter operation is finished in about ten or fifteen minutes if the pressing plate is maintained sufficiently hot. By selecting polished metallic pressing plates a very beautiful finish can be obtained at the same time. In this case Bakelite not only acts as impregnating and finishing material, but also as an excellent and permanent adhesive.

A modification of this method has given splendid results for veneering and finishing wood, accomplishing in a few minutes results which heretofore could not be obtained after weeks of polishing, sandpapering, and revarnishing with the older methods as practised by piano and furniture manufacturers.

A similar method may become useful for lining wooden or metallic boxes with impregnated asbestos so as to make them suitable for electrolysis tanks or storage batteries.

Whenever very thin layers of Bakelite have to be applied, it may be simpler to use A in alcoholic solution as a varnish; for this purpose, dissolved A, properly diluted with three to four times its volume of wood alcohol, is very suitable. This can be done by brushing, dipping, or spraying. This varnish dries in a few minutes to the point where it is no longer sticky, but it may take several hours before it is entirely dry. Even then the last traces of solvent are not expelled entirely, and even after years the layer remains A, soluble and fusible. If temperatures above 100° C. are applied, we may get nearer the stage C, but there is a decided tendency towards blistering, especially in such spots where the varnish has been applied rather thickly.

The use of the Bakeliser prevents all this, and for wood or other materials which have a porous surface it is entirely indispensable. For metallic surfaces, by using great precaution and thin layers, and by raising the temperature very gradually until it attains 120° to 140° C., a hard coating may ultimately be obtained.

Sheet iron or stamped boxes provided with a thin coating of Bakelite can stand boiling dilute sulphuric acids and boiling neutral solvents.

It should be borne in mind that, on account of the limited flexibility of Bakelite, such sheets can not be twisted or bent beyond certain limits without splitting the protective layer. In any such cases where bending has to be done, it must be done before the varnish is applied or after the A has been changed in B, which still leaves some scope for flexibility.

(To be continued)

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, June 24th, 1909.

Professor J. COSSAR EWART, Vice-President, in the Chair.

"On Pressure Perpendicular to the Shear Planes in Finite Pure Shears; and on the Lengthening of Loaded Wires when Twisted." By J. H. POYNTING, Sc.D., F.R.S.

"The Wave Motion of a Revolving Shaft and a Suggestion as to the Angular Momentum in a Beam of Circularly Polarised Light." By J. H. POYNTING, Sc.D., F.R.S.

"The Effect of a Magnetic Field on the Electrical Conductivity of Flame." By Prof. H. A. WILSON, F.R.S.

This paper contains an account of some experiments on the change in the conductivity of a Bunsen flame produced by a magnetic field. The current through the flame was horizontal, and the magnetic field was also horizontal, but perpendicular to the current. The ratio of the potential gradient in the flame to the current was taken as a measure of its resistance. The results show that $\delta R/R = AH^2 + BH$, where H denotes the magnetic field, R the resistance, and A and B are constants. The velocity of the negative ions can be calculated from the term AH^2 , and the result is 9600 cms./sec. for one volt per cm., which agrees with Mr. E. Gold's results obtained by an entirely different method. The term BH is presumably due to the upward motion of the flame gases, but its value is about fifty times greater than the value calculated from the ionic theory.

"Studies of the Processes Operative in Solutions. XI. The Displacement of Salts from Solution by various Precipitants." By Prof. H. E. ARMSTRONG, F.R.S., and Dr. J. V. EYRE.

"The Thermal Conductivity of Air and other Gases." By GEORGE W. TODD, M.Sc.

The paper gives an account of a determination of the thermal conductivities of air and other gases at atmospheric pressure. The conductivity was obtained from observations of the steady flow of heat between two horizontal circular metal plates maintained at different temperatures, the upper one at the temperature of steam and the lower one at room temperature. The upper plate was fixed, and the lower one could be moved up and down so as to vary the distance between them.

If the temperatures of the plates are kept constant, the quantity of heat passing per second from the upper plate to the lower, when the distance between them is x , is given by $Q = K/x + R + Ex$, where the constant K is proportional to the thermal conductivity, R is the heat radiated, and Ex is the effect due to the edge. The latter is negligible when x is small compared with the radius of the

plates, so that the relation between Q and x is given by a rectangular hyperbola. Hence the relation between Q and $1/x$ is a straight line, whose slope gives K , from which the conductivity is determined. The intersection of this line with the axis of Q gives the value R of the radiation.

The value of the conductivity so obtained was independent of the nature of the surfaces of the plates and also independent of the dimensions of the plates, the latter proving that convection currents were absent or negligible.

The conductivities of some gases other than air were determined by comparing the rates of flow of heat through them with the rate of flow through air when the plates were at a fixed distance apart.

The paper concludes with a calculation of the "radiation constant," from a determination of the absorption coefficient of the surfaces of the plates when painted black, and the radiation R .

"The Possible Ancestors of the Horses living under Domestication." Part I. By J. C. EWART, M.D., F.R.S.

"The Alcoholic Ferment of Yeast-Juice." Part IV. The Fermentation of Glucose, Mannose, and Fructose by Yeast-Juice." By ARTHUR HARDEN, F.R.S., and W. J. YOUNG.

1. Mannose behaves towards yeast-juice, both in the presence and in the absence of added phosphates, substantially in the same manner as glucose.

2. Fructose resembles both glucose and mannose in its behaviour, but in presence of phosphate is fermented much more rapidly than these sugars, and the optimum concentration of phosphate is much higher.

3. Fructose has the property of inducing rapid fermentation in presence of yeast-juice in solutions of glucose and mannose, containing such an excess of phosphate that fermentation is only proceeding very slowly. No similar property is possessed by glucose or mannose.

These properties of fructose indicate that this sugar when added to yeast-juice does not act merely as a substrate to be fermented, but bears some specific relation to the fermenting complex. All the facts are consistent with the supposition that fructose actually forms a part of the fermenting complex. When the concentration of this sugar is increased, a greater quantity of the complex would be formed, and, as the result of this increase in the concentration of the active catalytic agent, the juice would become capable of bringing about the reaction with sugar in presence of phosphate at a higher rate, and at the same time the optimum concentration of phosphate would become greater, exactly as is observed.

"The Electrical Reactions of certain Bacteria applied to the Detection of Tubercle Bacilli in Urine by means of an Electric Current." By CHARLES RUSS, M.B. (Lond).

The aim of these experiments was to ascertain whether bacteria suspended in an electrolyte are transmitted during electrolysis to either electrode, with a view to the recovery of pathogenic bacteria from a pathological fluid by such means.

During electrolysis of certain salts in which bacteria were suspended, the organisms were found to migrate to one electrode; in some instances there was no migration. The effect was noticed to occur with killed as well as with living bacteria.

By testing certain organisms in the same (but a small) series of electrolytes some differences of effect were found, though this line of enquiry was not pursued.

To utilise this bacterial movement, an electrolyte in which tubercle bacilli had shown marked cathodic aggregation was added to tuberculous urine, and the kathode arranged in the form of a bacterial trap. After electrolysis tubercle bacilli entered the trap, which was eventually withdrawn, and the organisms recognised in a stained film prepared from its contents. A series of such urines was tested in this way, and in each case tubercle bacilli were found in the trap.

In the final experiment a number of tubercle bacilli (estimated at 500) were added to 100 cc. normal urine, and

their detection attempted by separate investigators by means of the centrifuge and current. By the centrifuge none were found, while the current recovered 128 bacilli.

The results of this preliminary investigation may be summarised as follows:—Certain bacteria under the influence of a suitable current aggregate at one or other electrode. The aggregation varies with the nature of the electrolyte, and is probably due to affinity between the products of electrolysis and the bacteria. It occurs with killed as well as with living bacteria. The aggregation by electrical currents affords a means of collection and examination. The differences in behaviour of various bacteria are such as to suggest the possibility of utilising the method for purposes of specific discrimination; but in this particular the data hitherto obtained are not sufficient to warrant definite statements.

"The Effect of the Injection of the Intra-cellular Constituents of Bacteria (Bacterial Endotoxins) on the Opsonising Action of the Serum of Healthy Rabbits." By R. TANNER HEWLETT, M.D.

In this investigation, the effect of the endotoxins of the *Bacillus typhosus*, *Micrococcus pyogenes aureus*, and *B. tuberculosis* on the opsonising action of the serum of normal rabbits has been studied.

The endotoxins were prepared by the Macfadyen process, the rabbits were inoculated subcutaneously, and the specimens for counting the number of bacteria ingested by leucocytes were prepared in the usual manner. Human leucocytes were employed and the counts were made on fifty cells.

(A). *Typhoid Endotoxin*.—The results for this endotoxin are approximate only, as agglutination and bacteriolysis are complicating factors. The amount of endotoxin injected was 0.1 mgrm., prepared from an avirulent strain.

One day after injection a decided negative phase had developed (opsonic index about 0.2), two days after injection the index was rising (1.4) and attained a maximum on the third day (3.3), after which it fell. Dilution of the serum to 1 in 5 and 1 in 10 tended to increase phagocytosis.

(B). *Staphylococcus Endotoxin*.—Endotoxin prepared from an old laboratory strain in a dose of 0.1 mgrm. produced a rise in the opsonic index to 1.6, which persisted for some weeks. Endotoxin (0.1 mgrm.) prepared from a recently isolated strain produced a rise to 2.5. An equivalent dose of staphylococcus vaccine (1000 × 10⁶ cocci) produced a rise of the opsonic index to 1.8, which fell subsequently to a point lower than that with either endotoxin. Estimations of the opsonic indexes made with the recently isolated strain gave results higher than those obtained using the old strain. With another endotoxin, varying doses (0.1, 0.01, and 0.001 mgrm.) all produced marked rise in the opsonic indexes, the rise corresponding with the dose.

(C). *Tubercle Endotoxin*.—Injection of 0.002 mgrm. of endotoxin caused a rise in the opsonic index to 1.9 sixteen days after. A similar dose of German Tuberculin R. produced hardly any effect. A large dose (1.0 mgrm.) of endotoxin caused a marked negative phase (index 0.5) forty-eight hours after injection, with a subsequent rise to 1.8. Endotoxin (1.0 mgrm.) prepared from tubercle bacilli previously extracted with ether also produced a negative phase, with a subsequent rise to 1.5.

(D). *Keeping Power of Endotoxin Solutions*.—Experiments were performed with staphylococcus and tubercle endotoxin solutions which had been kept for seven weeks after preparation; there was little diminution in activity. Other experiments indicate that the solutions deteriorate but little for three to six months after preparation.

(E). "Negative Phase."—Experiments indicate that endotoxin produce decidedly less "negative phase" than a vaccine.

"On the Occurrence of Protandric Hermaphroditism in *Crepidula fornicata*." By J. H. ORTON.

"Sensitive Micro-balances and a New Method of Weighing Minute Quantities." Communicated by Sir William Ramsay, K.C.B., F.R.S. By B. D. STEELE and KERR GRANT.

"The Polarisation of Secondary γ -Rays." By Dr. R. D. KLEEMAN.

"On the Absorption of Homogeneous β -Rays by Matter, and on the Variation of the Absorption of the Rays with Velocity." By W. WILSON.

The experiments were made with a view to determining the manner in which the absorption coefficient of the β -rays varies with the velocity. Radium, which gives out rays whose velocities vary between very wide limits, was used as a source of radiation. A beam of rays from the radium passed into a magnetic field, by means of which approximately homogeneous rays could be brought into an electroscope. The velocities of the rays could be determined from the strength of the magnetic field. Screens of metal of different thicknesses were interposed in the path of the rays, and it was found that the law of absorption was not exponential, but approximately linear, except for large thicknesses of absorbing material. Various experiments were made to show that this was not due to the experimental arrangement, but was a real effect. The fact that the β -rays from uranium, actinium, &c., are absorbed by matter according to an exponential law is shown to be a proof not of their homogeneity, but of their heterogeneity. Groups of rays can be built up which represent the properties of these rays with respect to absorption. Further experiments were made on the change of velocity of the rays after passing through absorbing material, and it was found that the velocity of the rays, contrary to the view expressed by H. W. Schmidt, is appreciably reduced as they penetrate matter. The law of absorption of the β -particles when measured by the ionisation method involves a considerable number of factors, and, as might be expected, no simple relation could be found between the absorption of the rays and their velocity.

"Experimental Researches on Vegetable Assimilation and Respiration. V. A Critical Examination of Sachs' Method for Using Increase of Dry Weight as a Measure of Carbon Dioxide Assimilation in Leaves." By D. THODAY.

"The Reproduction and early Development of *Laminaria digitata* and *Laminaria saccharina*." By G. H. DREW, B.A.

"The Germicidal Action of Metals and its Relation to the Production of Peroxide of Hydrogen." By Dr. ALLAN C. RANKIN.

"Surface Flow in Calcite." By G. T. BEILBY, F.R.S.

"A Preliminary Note on *Trypanosoma eberthi* (Kent)—(*Spirochaeta eberthi*: Lühe) and some other Parasitic Forms from the Intestine of the Fowl." By C. H. MARTIN and Miss MURIEL ROBERTSON.

"The Spectrum of Magnesium Hydride." By Prof. A. FOWLER, A.R.C.S., F.R.A.S.

The author has previously discovered that many of the band lines peculiar to the sun spot spectrum are identical with lines composing the green fluting attributed to magnesium hydride by Liveing and Dewar. The present paper gives the results of a further investigation of this spectrum with high dispersion, together with details of wave-length determinations.

The principal results may be briefly summarised as follows:—(1) No sufficient reason has been found for modifying Liveing and Dewar's conclusion that the spectrum is produced by the combination of magnesium with hydrogen. (2) Lines are shown at short intervals in all parts of the spectrum from the extreme red to λ 2300, and definite groups of flutings begin at 5621.57, 5211.11, 4844.92, 4371.2, and near 2430. (3) From photographs of the magnesium arc in hydrogen at low pressures, taken with a 10-ft. concave grating, the positions of close upon 2000 lines composing the three principal bands have been

determined. The wave-lengths were derived from the interference standards of Fabry and Buisson, but have been corrected to Rowland's scale to facilitate comparison with solar spectra. (3) Twelve of the series of lines which compose the green band have been traced, and it is shown that none of the formulæ which have been proposed are sufficiently general in their application to represent all of these series within the limits of error of measurement. For the longer series the closest approximation is given by Halm's equation. (5) The identification of magnesium hydride in the sun spot spectrum has been fully confirmed, and is clearly demonstrated by photographs submitted for reproduction. (6) It is shown that many of the bright interruptions of the dark back-ground of the spot spectrum are not bright lines, but merely clear interspaces between lines or groups of lines in the spectrum of magnesium hydride. (7) The presence of the magnesium hydride flutings, together with flutings of titanium oxide and calcium hydride discovered at Mount Wilson, accords with the view that spots are regions of reduced temperature, and that their darkness is at least partly due to absorption. (8) The investigation of the possible presence of lines of magnesium hydride in the ordinary solar spectrum is for several reasons inconclusive, but there is evidence that very few, if any, of the thousands of faint lines tabulated by Rowland are to be accounted for by this substance.

"The Discovery of a Remedy for Malignant Jaundice in the Dog and for Redwater in Cattle." By Prof. G. H. F. NUTTALL, F.R.S., and SEYMOUR HADWEN.

"The Comparative Power of Alcohol, Ether, and Chloroform as Measured by their Action upon Isolated Muscle." By Dr. A. D. WALLER, F.R.S.

The Society adjourned over the Long Vacation to Thursday, November 4.

CHEMICAL SOCIETY.

Ordinary Meeting, June 17th, 1909.

Prof. HAROLD B. DIXON, F.R.S., President, in the Chair.

MESSRS. W. L. DUDLEY, A. H. ELLIOTT, and G. B. WALKER were formally elected Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Benjamin Leech, M.A., Beech Knoll, Macclesfield; Frederic William Robinson, B.Sc., Grove House, Farnworth, Widnes; Prof. Dr. Hermann Thoms, Berlin, Steglitz, Hohenzollernstr. 3; Everard Cecil Van Essen, 28, Hereford Road, Snaresbrook, N.E.

A Certificate has been authorised by the Council for presentation to ballot under By-law 1, Par. 3, in favour of A. K. Yegna Narayan Aiyer, M.A., Bangalore, India.

A ballot for the election of Fellows was held, and the following were subsequently declared duly elected:—Harold Edward Annett, B.Sc.; Harold Arnfield; John Gunning Moore Dunlop; John Harold Edge; Alfred Charles Glyn Egerton, B.Sc.; Harry Essex, jun.; Harold Hibbert, M.Sc., Ph.D.; Oswald Farquhar Kirby, M.A., B.Sc.; Hassum A. Lakhani, M.D.; Andrew Sneddon Matchet; Roland Josiah May; Thomas Napier; Norman Picton, B.Sc., Ph.D.; Herbert Charles Resker, B.A.; Fred. Robinson, B.A., B.Sc.; Barth. Frere Sawbridge, B.A.; Harry Sampson Wills; George James Woods.

Of the following papers, those marked * were read:—

*164. "The Carbonates of Copper and the Cupric carbonates." By SPENCER UMFREVILLE PICKERING.

Besides the mineral azurite, $3\text{CuO} \cdot 2\text{CO}_2 \cdot \text{H}_2\text{O}$ and the ordinary carbonate of copper, malachite, $2\text{CuO} \cdot \text{CO}_2 \cdot \text{H}_2\text{O}$, the following carbonates have been isolated:—

$5\text{CuO} \cdot 2\text{CO}_2$. A blue bulky precipitate, obtained by the precipitation of copper salts by sodium carbonate.

$5\text{CuO} \cdot 3\text{CO}_2$.—A light blue stable precipitate, obtained by precipitation with sodium hydrogen carbonate,

$8\text{CuO}_3\cdot 3\text{CO}_2\cdot 6\text{H}_2\text{O}$.—A rather dark blue substance obtained by the action of water on the double carbonate of copper and sodium.

All the basic carbonates are insoluble in water and in sodium carbonate solution, but they dissolve slightly in aqueous carbonic acid and in acid carbonates, a normal copper carbonate, or a double carbonate of copper and the alkali metal, being formed. The latter is obtained as a molecular compound in rather light blue crystals from such solutions, although in the solutions it is present in another form, as sodio-cupric carbonate, of the constitution $\text{NaO}\cdot\text{CO}\cdot\text{OCuO}\cdot\text{CO}\cdot\text{NaO}$. In this compound the copper is electro-positive, but has a colour thirty times more intense than the copper in copper sulphate. When excess of sodium carbonate is added to it, the copper becomes electro-negative, and has a colour eighty times more intense than that in copper sulphate. The substance then present is an α -cupricarbonate, consisting of $\text{Na}_2\text{Cu}(\text{CO}_3)_2$ united with Na_2CO_3 , but in which the copper is joined to the carbon atoms, and is in a quadrivalent condition. It oxidises dextrose, and the constitution suggested represents the presence of a loosely combined oxygen atom explaining such a reaction. Excess of sodium hydroxide decomposes it, but a greater excess dissolves the precipitated basic carbonate to form a deep violet-blue solution of the β -cupricarbonate, which consists of $\text{Na}_2\text{Cu}(\text{CO}_3)_2$ united with 1 or 2 NaOH . This, too, oxidises dextrose, and also combines with cellulose. It is stable in presence of excess of alkali, whereas the α -compound gradually decomposes, either into the crystalline double salt or into malachite. The sodio-cupric carbonate decomposes in a similar manner.

DISCUSSION.

Mr. W. C. REYNOLDS expressed the opinion that, although it was possible to give to the double carbonates the structural formula which the author had done, they did not afford a satisfactory explanation, since certain of the double succinates (*Trans.*, 1898, lxxiii., 703), which were exactly analogous, and exhibited the same behaviour in solution, had the composition $\text{K}_4\text{R}(\text{C}_4\text{H}_4\text{O}_4)_3$, where R is Cu or Co. Such compounds could not be formulated in the way described by the author, and it appeared probable that the constitution of the cupricarbonate could be explained by molecular association with water of crystallisation, thus involving the idea of quadrivalent oxygen.

Mr. W. A. DAVIS suggested that in assigning structures to the mixed or double carbonates, the water of crystallisation probably ought to be considered; he had previously shown that the so-called trihydrate of magnesium carbonate, $\text{MgCO}_3\cdot 3\text{H}_2\text{O}$, was in reality a hydrated hydroxy-carbonate, $\text{OH}\cdot\text{MgCO}_3\cdot \text{H}_2\text{O}$ (*Journ. Soc. Chem. Ind.*, 1906, xxv., 788), and had ascribed the impossibility of preparing normal copper carbonate by precipitation to the great tendency to the formation of mixed alkali copper carbonates, the hydrolysis of which gave rise to basic carbonates. In the case of magnesium he had succeeded in giving a proof that the very numerous "basic carbonates" were really mixtures of three compounds, $\text{OH}\cdot\text{MgCO}_3\cdot \text{H}_2\text{O}$, $\text{OH}\cdot\text{MgCO}_3\cdot \text{H}_2\text{O}$, and $\text{Mg}(\text{OH})_2$, in varying proportions. In the case of copper there was slender evidence as to the existence of definite basic carbonates other than malachite and azurite.

Mr. E. H. JEFFERS asked if Mr. Pickering considered the formula given for the α -cupricarbonate was analogous to Fehling's blue salt, because in the latter the copper had been shown to be in the electro-positive condition.

He was inclined to think that these compounds were simply molecular aggregates, in which the alkali hydroxide took the place of water of hydration. For instance, the corresponding citric acid compound was a peculiar peacock-green colour, easily reduced by sugar, but on addition of a little alkali hydroxide one obtained an intensely blue solution, exactly similar to Fehling's blue salt.

Moreover, more than one salt could be prepared from

Fehling's solution, but on shaking the latter with alcohol, separating, and washing for hours with alcohol, the blue compound obtained was strongly alkaline.

Mr. PICKERING said, in reply, that since the cupricarbonates could not be isolated, the formulæ given for them must be regarded only as suggestions. Very probably they were symmetrical, which, in the case of the α -compound, would involve the combination of $3\text{Na}_2\text{CO}_3$ with every CuCO_3 , as suggested by Mr. Reynolds. The constitution of Fehling's solution had not been investigated, beyond ascertaining that its oxidising properties depended on the presence of electro-negative copper. The nature of the action between cellulose and the β -cupricarbonate was not clear, but the former appeared to be unaffected by it after the copper was removed.

*165. "Isoquinoline Derivatives. Part I. Oxidation of Laudanosine." By FRANK LEE PYMAN.

Just as narcotine and hydrastine yield on oxidation opianic acid together with cotarnine and hydrastinine respectively, so laudanosine (N-methyltetrahydropapaverine) yields veratraldehyde and a new base, 4 : 5-dimethoxy-2- β -methylaminoethylbenzaldehyde, $\text{C}_{12}\text{H}_{17}\text{O}_3\text{N}$. The chemical behaviour of this compound is very similar to that of cotarnine; it is colourless, but yields primrose-coloured salts, derived from 6 : 7-dimethoxy-2-methyl-3 : 4-dihydroisoquinolinium hydroxide by substitution. The addition of aqueous potassium cyanide to a solution of the chloride precipitates 1-cyano-6 : 7-dimethoxy-2-methyltetrahydroisoquinoline, $\text{C}_{13}\text{H}_{16}\text{O}_2\text{N}_2$, and boiling aqueous sodium hydroxide converts the aldehyde-base into the anhydrides of the corresponding acid and alcohol, 1-keto-6 : 7-dimethoxy-2-methyltetrahydroisoquinoline, $\text{C}_{12}\text{H}_{15}\text{O}_3\text{N}$, and 6 : 7-dimethoxy-2-methyltetrahydroisoquinoline, $\text{C}_{12}\text{H}_{17}\text{O}_2\text{N}$. The aldehyde-base yields an acetone condensation product, bis(4 : 5-dimethoxy-2- β -methylaminoethylbenzylidene)acetone, $\text{C}_{27}\text{H}_{36}\text{O}_5\text{N}_2$.

*166. "The Colour and Constitution of Azo-compounds." By JOHN THEODORE HEWITT and WILLIAM THOMAS.

Further information regarding the colour exhibited by doubly substituted azo-compounds has been collected, and the following substances have been examined :—

1. *p*-Acetylaminobenzeneazophenol.
2. *p*-Aminobenzeneazophenol and its dihydrochloride.
3. *p*-Dimethylaminobenzeneazophenol; its mono- and dihydrochlorides and acetyl derivative.
4. *p*-Trimethylammonium iodide-benzeneazophenol.
5. *p*-Dimethylaminobenzeneazoanisole.
6. *p*-Trimethylammonium iodide-benzeneazoanisole.

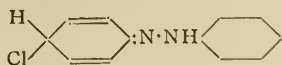
Substances 2, 3, 4, 5, and 6 give yellow solutions in neutral solvents; 2, 3, and 5 give red or magenta solutions in dilute hydrochloric acid (formation of monohydrochloride), whilst in concentrated hydrochloric acid the solutions become orange in colour (dihydrochloride—oxonium salt).

Solutions 4 and 6 remain yellow in dilute acid, but give orange solutions like the other substances in concentrated acid.

DISCUSSION.

Mr. BALY pointed out that there seemed to him to be certain objections to Dr. Hewitt's explanation of the origin of the increased absorption of the hydrochlorides of the substituted azo-compounds. In the first place, it must be remembered that the addition of hydrochloric acid, if it be added to the molecule in the way suggested, must decrease the residual affinity of the molecule, and therefore it was difficult to understand how the absorption could thereby be increased, since the amount of absorption depended directly on the residual affinity of a compound. In the second place, the quinonoid structure advanced by Dr. Hewitt would not be expected to have so decidedly a deeper colour than the parent substance, since Mr. Tuck had shown that although there was a difference between the two isomeric compounds, $\text{C}_6\text{H}_5\cdot\text{N}:\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{OBz}$ and $\text{C}_6\text{H}_5\cdot\text{NBz}\cdot\text{N}:\text{C}_6\text{H}_4\cdot\text{O}$, yet this difference was in no way comparable with that between hydroxyazobenzene and its

hydrochloride. In the third place, since azobenzene itself gave a hydrochloride far more deeply coloured than the parent substance, it would appear that any explanation of the colour of the hydrochlorides of the substituted azo-compounds must also be capable of explaining the similar phenomenon as observed with azobenzene itself. It was true that an analogous structure for azobenzene hydrochloride might be written :—



but this appeared to be improbable.

About a year ago Miss Marsden and he showed that the aminoaldehydes and -ketones of the aromatic series displayed a great increase in absorption in the presence of a small quantity of hydrogen chloride in alcoholic solution, although the true hydrochlorides were colourless. Dr. Lapworth had suggested that this increase in colour might be due to the formation of an electro-positive ion ;

for example, $\text{CHO} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_3^+$, where the nitrogen atom was quinquivalent, and so possessed an increased residual affinity. The hydrochloride (undissociated) would naturally be colourless, owing to the entire removal of the residual affinity of the amino-group. He (the speaker) suggested that possibly some analogous condition might obtain with the azo-grouping, and that a positive ion might be formed, thus, $\text{C}_6\text{H}_5 \cdot \text{NH}^+ \cdot \text{N}^+ \cdot \text{C}_6\text{H}_5$. The residual affinity of the azo-linking would then be increased, and the suggestion would have the merit of applying equally well to azobenzene and its substituted derivatives.

Dr. HEWITT, in reply, said that Dr. Lapworth's observation that the addition of alcoholic hydrochloric acid to alcoholic aminoazobenzene first produced an orange colour which afterwards turned purple, might be due to the transitory production of a salt of benzeneazophenylammonium, which was afterwards transformed into the quinonoid salt.

Mr. Baly's objection to the quinonoid formulæ for the salts was not supported by the chemical facts. Free benzeneazophenol behaved as a hydroxylic aromatic compound towards substituting agents, but in its salts with acids, the original phenolic nucleus resisted the action of nitric acid, but now was easily substituted in the other nucleus as if it were an anilide or hydrazone. Similar arguments could be brought forward with regard to the aminazo-compounds.

*167. "Studies of Dynamic Isomerism. Part IX. The Relationship between Absorption Spectra and Isomeric change. Absorption Spectra of Sulphonic Derivatives of Camphor." By THOMAS MARTIN LOWRY and CECIL HENRY DESCH.

The band which is present in the absorption spectrum of α -bromocamphor appears also in the spectra of the ammonium π -sulphonate, the π -sulphonamide, and the acetyl derivative of this amide. It is also observed in the potassium β -sulphonate, the β -sulphonamide, the β -sulphonanhydramide, and the sulphopiperidine (m. p. 75°) derived from α -bromocamphor, but disappears when the two α -hydrogen atoms are displaced by halogens, as in dibromocamphor β -sulphonanhydramide. In the case of α -chlorocamphor, the band is also absent from the spectrum of the mono-substituted anhydramide, although it is developed by the β -sulphonamide and the potassium β -sulphonate. In the case of camphor and α -methylcamphor, the sulphonic acids and their salts give rise to a band, but the amide and anhydramide give continuous absorption curves. The absorption bands of the alkali-sulphonates are weakened by the addition of an excess of alkali, although this is an essential condition for bringing about isomeric change.

168. "Isoiminazolone." By HENRY JOHN HORSTMAN FENTON and W. A. R. WILKS.

When dry dihydroxymaleic acid is intimately mixed with excess of carbamide and the mixture is heated to 100°, three distinct products are obtained ; one of these is a compound which is sparingly soluble in water, crystallises in the tetragonal system, and gives an intense red colour with ferric chloride. Analysis and molecular-weight determination show that this compound has the formula $\text{C}_3\text{H}_4\text{ON}_2$, and its mode of formation suggests the con-

stitution, $\begin{array}{c} \text{CH-NH} \\ \parallel \\ \text{CH-NH} \end{array} \text{CO}$. It appears, however, to differ notably in many respects from the " μ -iminazolone" obtained by Marckwald and Ellinger (*Ber.*, 1892, xxv., 2357).

When evaporated with chlorine water, or with hydrochloric acid and a trace of potassium chlorate, isoiminazolone leaves a brilliant pink residue, which is changed to violet by ammonia. Its behaviour in this respect is indeed closely analogous to that of uric acid or xanthine, and it is considered probable that erroneous conclusions may have been arrived at by former investigators in placing too much reliance on this colour reaction as indicative of purine derivatives.

169. "Homologues of Furfuraldehyde." By HENRY JOHN HORSTMAN FENTON and F. ROBINSON.

The halogen derivatives of methylfurfuraldehyde are readily obtained by the action of dry halogen acids on ketohexoses, such as laevulose, or on various forms of cellulose (compare Fenton and Gostling, *Trans.*, 1899, lxxv., 423 ; 1901, lxxix., 807). The authors have studied the application of the Friedel and Crafts' reaction in effecting syntheses by these halogen derivatives, and further evidence is brought forward in support of the constitution previously assigned to these compounds.

Benzylfurfuraldehyde, $\begin{array}{c} \text{O} \\ \diagdown \\ \text{C}(\text{CH}_2\text{Ph}) : \text{CH} \\ \diagup \\ \text{C}(\text{CHO}) = \text{CH} \end{array}$, obtained by

the interaction of chloromethylfurfuraldehyde and benzene in presence of aluminium chloride, crystallises in large colourless prisms, which melt at 31°. The benzylphenylhydrazone and the oxime are colourless and crystalline, and the latter has been obtained in two stereoisomeric forms.

Chloromethylfurfuraldehyde is easily oxidised by means of dilute nitric acid, yielding a dibasic acid, $\text{C}_4\text{H}_2\text{O}(\text{CO}_2\text{H})_2$, which is identical with furan-2:5-dicarboxylic acid (dehydromucic acid).

170. "The Relation between the Strengths of Acids and Bases, and the Quantitative Distribution of Affinity in the Molecule." (Part II.). By BERNHARD FLÜRSCHHEIM.

In Part I. (*Trans.*, 1909, xcv., 718), it was mentioned that a few amines had affinity values which were not in agreement with the theory then published. In order to determine these anew, it was first necessary to improve Farmer and Warth's distribution method, since the results obtained by these authors sometimes differ considerably from those obtained by other methods, a fact which has been attributed by Lunden to possible association. Two new ways for determining volatile amines in the benzene layer have been worked out, one consisting in distilling off the benzene in a current of dry hydrogen chloride, and heating the residue in a current of the same gas ; the other, in retaining the amine by a weighed amount of picric acid. The latter method was shown to reduce the experimental error to less than 1 mgrm. Determinations in very dilute solution were thus rendered possible, giving, for *m*-toluidine, for instance, results in agreement with those obtained by Bredig by the conductivity method. In this way, the halogen-substituted anilines, previously disagreeing with the theory, were found to be in perfect harmony with the same, and thus to constitute another experimental proof in its favour.

(To be continued).

NOTICES OF BOOKS.

Dustless Roads Tar Macadam. By J. WALKER SMITH. London: Charles Griffin and Company, Ltd. 1909.

THE solution of the new problem which has arisen owing to the increase in the number of motor propelled vehicles on English roads is being energetically sought, and this summary of the practical results obtained with a macadam provided with a bituminous binding is a valuable contribution to the literature of the subject. Besides discussing the methods of preparing and laying tar macadam, and different modifications of the process of tar spraying, the book contains a collection of the opinions of engineers to counties, boroughs, &c., in answer to questions relating to the advantages and disadvantages of tar macadam, the cost of the process, and the durability of the paving under different circumstances. The author has given in tabulated form the replies received, and in addition he has carefully summarised the answers and discussed the general trend of opinion. It is not astonishing that much diversity of views was exhibited with regard to the foothold and durability of tar macadam, and this alone shows the necessity for a more thorough study of the question by engineers and others interested in road making, a study which they will do well to commence by reading this book.

Low Temperature Research at the Royal Institution of Great Britain. II. The Charcoal Vacuum Septenate. By Prof. HENRY EDWARD ARMSTRONG. London: Wm. Clowes and Sons, Ltd. 1909.

THIS essay gives a summary of the work carried out at the Royal Institution during the years 1900-1907. The author describes this period as the charcoal vacuum septenate in low temperature research, since it has seen the application of the absorptive power of charcoal for gases at low temperatures. This process has been found exceptionally valuable, and has led to results of great importance. The history of the investigation of the absorptive power of charcoal forms an interesting introduction to the description of the experimental details of the method of obtaining vacua by means of highly cooled charcoal, the different forms of apparatus which have been perfected being fully illustrated. The absorption of mixtures of gases is shortly treated, and a discussion of the properties and structure of charcoal leads to the establishment of the proof that the molecule of amorphous carbon has an ethenoid structure. The results which have been obtained as regards the alteration in the properties of materials at low temperatures are also explained, and the essay concludes with a short account of the general outcome of the researches which have already been carried out at the Royal Institution, and of the need for extended research and increased expenditure for the purpose.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlviii., No. 21, May 24, 1909.

Solubility of Lead Sulphate.—J. Sehnal.—The author's determinations of the solubility of lead sulphate give numbers which differ considerably from those obtained by Fresenius and Rodwell. The purity of the salt is the only factor which can influence the solubility, the presence of a trace of sulphuric acid being sufficient to cause a considerable difference. Solution takes place extremely slowly, and possibly the lead sulphate decomposes according to the equation $\text{PbSO}_4 + 2\text{H}_2\text{O} = \text{PbOH}_2\text{O} + \text{H}_2\text{SO}_4$. The hydrated oxide of lead dissolves easily in sulphuric acid.

Atomic Weight of Phosphorus.—G. Ter Gazarian.—The determination of the atomic weight of phosphorus by

chemical methods is attended by great difficulties, and the better way is to find the density of a gas rich in phosphorus, e.g., hydrogen phosphide, and hence deduce the molecular weight. A correction has to be applied for the deviation from Avogadro's law. The mean value of the atomic weight thus found is 33.930, which gives 30.906 as the atomic weight of phosphorus if $\text{H} = 1.008$. This value, 30.906 is the same as that obtained by Bernoulli by calculations based on the constitution of the chemical elements.

Synthesis of Derivatives of Racemic Fenone.—L. Bouveault and M. Levallois.—The chloride of dihydrocamphonic acid condenses with benzene in presence of aluminium chloride, giving 3-benzoyl-1-isopropylcyclopentane, from which by methylation 3-benzoyl-3-methyl-1-isopropylcyclopentane is obtained. The amide obtained from this acetone by the action of sodamide resembles the natural racemic amide in appearance and solubility, but it fuses at 109° instead of at 116° , and all attempts to raise the melting-point by fractional crystallisation have been unsuccessful. Both active amides fuse at 94° , and probably the synthetic amide is a mixture of the racemic amide and an isomer, this mixture being difficult to separate into its constituents.

Cyclisation of Ketone Acids.—E. E. Blaise and H. Koehler. The cyclisation of ketone acids always occurs at one of the carbon atoms near the ketone function. Cyclic chains containing C_5 and C_6 are most easily formed. If two closed chains, one containing C_4 and the other C_6 , are possible, the C_6 chain is the one formed. Similarly of C_5 and C_7 chains the former is always obtained, while if C_6 and C_8 chains are possible the one formed contains C_6 . If the chain formed must contain at least C_7 no cyclisation occurs.

Berichte der Deutschen Chemischen Gesellschaft,
Vol. xlii., No. 8, May 22, 1909.

Optical Activity of Natural Petroleum.—M. Rakusin.—Walden ascribed the optical activity of petroleum to the influence of the earth's magnetism, supposing that the deflection of the plane of polarisation instead of being merely a temporary character has in the course of the enormously long geological periods become a permanent property. According to this view a correction would have to be applied in all polarimetric observations for the effect of the earth's magnetism. The author, however, regards Walden's view as most probably incorrect, for the active petroleum is accompanied by inactive waters which have been subjected to the same influence, and he thinks that the cause of the activity is the asymmetric structure of the hydrocarbon molecule of which petroleum is composed.

Penetration of Gases through Glass.—Alfred Stock and Hans Heynemann.—A piece of silver foil was placed in a flask of ordinary glass, which was then exhausted. It was then left in a closed vessel in which iodine crystals were present. After three months nitric acid was added in order to see whether the silver dissolved completely, or whether any silver iodide had been formed owing to the penetration of the iodine vapour through the glass. It was found that there was no trace of iodide formed, and thus the statement of Zengheli to the effect that many gases or vapours of solid substances can pass through glass at the ordinary temperature appears to be incorrect.

Use of Mercury Cathodes.—Wilhelm Böttger.—From the author's experiments on the use of mercury cathodes in the electrolytic separation of mercury from zinc it appears that the method is accurate and convenient. It can also be employed for other metals, e.g., chromium. It is essential that the temperature of the contents of the cell should not rise too high, i.e., too great a current strength must not be used. For vessels of ordinary dimensions 2 ampères (corresponding to 28 amp. per sq. cm.) produces differences of about 0.4 mgrm. It is best not to allow the current strength to rise above 1 amp., and to let the electrolysis last from ten to fifteen minutes.

THE CHEMICAL NEWS.

Vol C., No. 2590.

THE RADIUM AND URANIUM CONTAINED IN RADIO-ACTIVE MINERALS.

By Mdle. ELLEN GLEDITSCH.

It is generally admitted that there is a constant relation between the uranium and radium in radio-active minerals.

Various researches have led to this result. McCoy (*Ber.*, 1904, xxxvii., 2641) determined the intensity of the α -rays, and Eve (*American Journal Science*, xxii., 4 and 477) the intensity of the γ -rays emitted by minerals the uranium in which had been previously determined. Taking into account the properties of the rays emitted by radium and its decay products, they concluded that the ratio between the uranium and radium was constant. Moreover, Strutt (*Proc. Roy. Soc.*, 1905, A, lxxvi., 88) and Boltwood (*Am. Journ. Sci.*, xviii., No. 104; *Phil. Mag.*, April, 1905) determined the quantity of radium contained in the minerals by measuring the amount of emanation disengaged. Boltwood made the most thorough examination. He determined the uranium in a great number of minerals; then he treated a small quantity of the mineral with acids; the emanation thus set free was introduced into a condenser where the ionisation produced by it could be measured after two or three hours. Finally, by comparing this power of ionisation with that produced by the emanation disengaged from a solution of pure radium of known strength, Rutherford and Boltwood (*Am. Journ. Sci.*, xx., July, 1905; xxii., July, 1906) were able to give an absolute value for the quantity of radium in equilibrium with 1 gm. of uranium in the radio-active minerals. This number is 3.4×10^{-7} (Boltwood, *Am. Journ. Sci.*, xxv., April, 1908).

Although objections may be made to the method employed, Boltwood's results are regarded as very reliable owing to the concordance of the results obtained for minerals of very different origin and composition, and the confirmation of them by the researches already mentioned of Strutt, Eve, and McCoy. Boltwood ought to have made a correction for the disengagement of emanation lost by the minerals before they were dissolved, a correction which is sometimes fairly large (Boltwood, *Phil. Mag.*, April, 1905). Then the question arises whether all the emanation contained in a mineral can be set free at the moment of solution. It might be supposed, for example, that in a mineral which contains sulphides the action of the nitric acid would lead to the formation of sulphates of barium and lead, which would precipitate the sulphate of radium, and thus cause a loss of emanation. This objection has been put forward by Boltwood himself (*Am. Journ. Sci.*, xviii., No. 104).

The question of the relation between the uranium and radium in radio-active minerals being of great importance, I undertook a research on the subject.

I determined the amount of radium present by another method which differs from the above in that it enables the radium to be separated from the mineral and estimated separately. It consists in dissolving a relatively large amount of mineral, 40 to 100 grms., adding a little barium chloride, and precipitating with sulphuric acid. The sulphates of barium, radium, and lead thus obtained were transformed by boiling with a mixture of sodium carbonate and soda; thus the greater part of the lead was removed and filtration was facilitated. The contents were then dissolved in dilute hydrochloric acid. In this solution the radium was determined by the emanation set free by the method actually employed in Mdme. Curie's laboratory.

The minerals were dissolved in different acids; when they left residues I treated these separately until I had either the whole in solution or had obtained an inactive

residue. In the solutions I added barium chloride several times, and then I precipitated the sulphates until the precipitates were no longer active or did not contain an appreciable amount of radium.

By taking suitable precautions for each mineral and working carefully, the first precipitate may be made to contain nearly all the radium. Several analyses were performed for each mineral, and they gave very concordant results.

After the elimination of the radium the uranium was determined in the solution by methods which were applicable for the different minerals.

When I calculated the ratio radium—uranium, I found that it is not constant for the following minerals—a French autunite, a Joachimsthal pitchblende, and a thorianite from Ceylon. Without giving in detail the numbers obtained for the different minerals, I need only say that I obtained for pitchblende a number which agreed with that given by Boltwood, while autunite gave a lower and thorianite a higher value; the amount of radium associated with 1 gm. of uranium was thus less in autunite and greater in thorianite.

In the case of autunite the objection might be raised that it is a secondary mineral, formed perhaps from an active primary mineral by different geological processes. It may be remembered that some pyromorphites containing no uranium contain appreciable amounts of radium (J. Danne, *Comptes Rendus*, 1905, cxl., 241), a fact which has been explained as being due to a chemical separation caused by water. It seems more difficult to find an explanation for the difference between pitchblende and thorianite.

I am now engaged in examining further into the method employed to find out whether there are reasons which can explain the difference between Boltwood's results and mine. Meanwhile I am extending my study to other minerals.—*Comptes Rendus*, cxlviii., 1451.

SIXTEENTH ANNUAL REPORT OF THE COMMITTEE ON ATOMIC WEIGHTS. DETERMINATIONS PUBLISHED DURING 1908.

By F. W. CLARKE.

DURING the calendar year 1908 a moderate number of investigations upon atomic weights have been published, but the total output is not large. The data are summarised in the following pages, together with a few items dated 1907, which were not accessible until after the publication of the report for that year.

Chlorine.—Noyes and Weber effected the complete synthesis of hydrochloric acid, weighing the hydrogen in palladium and the chlorine in the form of potassium chloroplatinate (*Journ. Am. Chem. Soc.*, xxx., 13). The hydrochloric acid produced by passing the hydrogen over the heated chloroplatinate was also collected and weighed. In one series of experiments the acid was directly collected by absorption in water; in the second series, previous to absorption, it was condensed to the solid form. For details the original paper must be consulted; only the following final results, with all corrections applied, can be given here first on the basis of H = 1.

Series I.					
Weight H.	Weight Cl.	Weight HCl.	At. wt. Cl.	Mol. wt. HC	
0.25394	8.93293	9.18695	35.177	36.178	
0.28004	9.85590	10.13259	35.195	36.183	
0.51821	18.23468	18.75359	35.188	36.189	
0.67631	23.79587	24.47123	35.186	36.185	
0.58225	20.48158	—	35.177	—	
0.47989	16.88423	17.36310	35.184	36.182	
0.64132	22.55816	23.20054	33.175	36.176	
Mean			35.183	36.181	

Series II.

Weight H.	Weight Cl.	Weight HCl.	At. wt. Cl.	Mol. wt. HCl.
0.81608	28.71691	29.53167	35.188	36.187
0.83194	29.28055	30.11207	35.195	36.195
0.39074	13.74926	14.14078	35.187	36.188
0.75560	26.58427	27.33926	35.183	36.182
0.77518	27.26746	28.04110	35.177	36.175

Mean 35.186 36.185
Mean of all . . . 35.184 36.183

With $H = 1.00762$, $Cl = 35.452$. With $H = 1.00787$ (Noyes), $Cl = 35.461$. The authors adopt 35.457 as the most probable value.

Edgar's syntheses of hydrochloric acid were differently conducted (*Phil. Trans.*, ccix., A, 1). The hydrogen was weighed in palladium, but the chlorine was taken directly in the liquid form, having been prepared by the electrolysis of fused silver chloride. The chlorine was burned at the end of a quartz tip in an atmosphere of hydrogen, and the hydrochloric acid was also weighed. In three experiments the acid was condensed to solid and so weighed; in two others it was weighed after absorption in water. The corrected data are as follows; with $H = 1$:—

Weight H.	Weight Cl.	Weight HCl.	At wt. Cl.	Mol. wt. HCl.
2.1452	75.5026	77.6469	35.196	36.196
2.0387	71.7504	73.7880	35.194	36.194
1.7762	62.5004	—	35.188	—
1.9935	70.1638	72.1565	35.196	36.196
1.6469	57.9671	—	35.198	—
2.1016	73.9662	—	35.195	—
1.7254	60.7162	62.4401	35.190	36.189
2.0885	73.4991	75.5859	35.192	36.191

Mean 35.194 36.193

With $H = 1.00762$, $Cl = 35.462$ and 35.461 , in close agreement with the former work of Dixon and Edgar. This is higher by 0.01 than the determinations of Noyes and Weber.

There is also a preliminary note by Gray on the density and volumetric composition of HCl (*Proc. Chem. Soc.*, xxiv., 215; additional work on Cl by Guye and Fluss and by Oechsner de Coninck was received too late for use in this year's report). Twenty determinations gave for the weight of a normal litre of the gas the value 1.63885 grms. It was then analysed volumetrically by passage over heated aluminium, and measurement of the volume of hydrogen set free. The ratio thus found is $H_2 + HCl = 1.00790$. From these data, combined with Morley's figures for the density and atomic weight of hydrogen, $Cl = 35.453$. The details of the investigations are yet to be published.

Nitrogen.—Guye and Pintza (*Comptes Rendus*, cxlvii., 925) have determined the density of the gaseous mixture $N_2 + 3H_2$ produced by the decomposition of $2NH_3$. The corrected weight of a normal litre is given as 0.37989 gm. Combining this with the densities of nitrogen and hydrogen they find that the volume ratio $N : 3H = 1 : 3.0072$. Hence, if $H = 1.0076$, $N = 14.014$. The authors attach little importance to this determination, but regard it as having corroborative value.

(NOTE.—The work of Guye and his colleagues upon the atomic weight of N has recently been published in collected form. See *Mém. Soc. Phys.*, &c., de Genève, v., 35, fascicule 4; see also Leduc, *Comptes Rendus*, cxlvi., 399, on the atomic weights of N, O, and C).

Sulphur.—Baumé and Perrot (*Journ. Chim. Phys.*, vi., 610) have determined with great care the density of hydrogen sulphide. (In an earlier paper, *Journ. Chim. Phys.*, vi., 1, Baumé gives density and critical determinations for SO_2 , $(CH_3)_2O$, and CH_3Cl). From eighteen determinations they find the weight of a normal litre of the gas to be 1.5392 grms. Reducing this by means of the critical constants the atomic weight of sulphur becomes

$S = 32.070$, in good agreement with the chemical determinations by Richards and Jones.

Lead, Zinc, and Cadmium.—In a thesis published in 1907, but only recently received, Luigi Meaglia gives approximate determinations of the atomic weights of lead, zinc, and cadmium (*Thesis*, University of Grenoble, 1907). His method consisted in precipitating metallic silver or gold from suitable solutions by known weights of the three metals under consideration. For lead, two sets of values are given, representing two preparations of the metal. With these, silver was thrown down from silver nitrate solutions, and weighed. With $Ag = 107.93$ the following values for Pb were obtained :—

Series I.	Series II.
206.872	206.866
206.907	206.897
206.903	206.927
206.909	206.933
206.930	206.935
206.903	—
206.929	—

By means of zinc, silver was thrown down from a sulphate solution, and gold from a solution of sodium chloraurate. With $Ag = 107.93$ and $Au = 197.2$ the subjoined values for Zn were found :—

Silver series.	Gold series.
65.58	65.509
65.45	65.424
65.50	65.440
65.41	65.470

With cadmium, two similar series of determinations were made, giving for Cd the following values :—

Silver series.	Gold series.
112.37	112.41
112.56	112.45
112.45	112.65
112.38	112.47
—	112.48
—	112.40
—	112.42
—	112.41

These determinations, as the author admits, are only crude approximations. Still they have some corroborative significance.

The atomic weight of cadmium has also been determined by Blum, who converted the oxide into the sulphide by heating in a current of hydrogen sulphide (*Thesis*, University of Pennsylvania, 1908). His figures, with vacuum weights, are as follows :—

Weight CdO.	Weight CdS.	Atomic weight.
1.80552	2.03108	112.62
0.66349	0.74617	112.88
1.82460	2.05256	112.54
1.88424	2.11974	112.50
3.59206	4.04081	112.55
4.38093	4.92695	112.86

These results are discordant and entitled to very little consideration. Blum also tested several other methods of determination, and found them to be unsatisfactory. When silver was precipitated by cadmium from a nitrate solution, silver nitrite was formed, and the precipitate contained some cadmium.

Bismuth.—Three papers upon the atomic weight of bismuth have been published by Gutbier, in collaboration with Birckenbach, Mehler, and Janssen (*Journ. Prakt. Chem.*, lxxvii., 457; lxxviii., 409 and 421). The data had previously appeared in Inaugural Dissertations by the three collaborators, and are given in my reports for 1906 and 1907.

Tellurium.—In a paper upon the homogeneity of tellurium Lenher (*Journ. Am. Chem. Soc.*, xxx., 741) has given one analysis and one synthesis of TeO_2 as follows:—

0.85635 TeO_2 gave 0.6845 Te. Hence $\text{Te} = 127.52$.
0.1694 Te gave 0.2119 TeO_2 . Hence $\text{Te} = 127.55$.

These figures represent different fractions of the material investigated.

(NOTE.—For a criticism of Marckwald's work on tellurium, see Baker, CHEMICAL NEWS, xcvi., 209).

Rhodium.—Hüttlinger (Inaugural Dissertation, Erlangen, 1907), in order to determine the atomic weight of rhodium, reduced chloropentamminrhodium chloride by heating in hydrogen. His figures, which are preliminary in character, are as follows:—

Weight chloride.	Weight Rh.	Atomic weight.
1.60574	0.56124	102.906
1.67310	0.58492	102.943
1.30182	0.45507	102.925
Mean		102.925

This value is identical with that previously found by Seubert and Kobbe.

Palladium.—Atomic weight re-determined by Haas, who reduced palladosammine bromide by heating in hydrogen (Inaugural Dissertation, Erlangen, 1908). The results obtained, with vacuum weights, were as follows:—

Weight bromide.	Weight Pd.	Atomic weight.
2.06470	0.73274	106.73
1.73455	0.61563	106.75
2.64773	0.93978	106.76
1.29106	0.45821	106.74
2.26758	0.80490	106.77
1.90770	0.67704	106.74
1.77729	0.63082	106.76
Mean		106.75

The calculations were made with $\text{Br} = 79.953$, $\text{N} = 14.037$, and $\text{H} = 1.008$. Recalculated with $\text{Br} = 79.92$, $\text{N} = 14.01$, and $\text{H} = 1.008$, $\text{Pd} = 106.69$.

These figures are in close agreement with those found by Amberg, Krell, and Woernle. Much lower values were obtained by Kemmerer, who reduced palladosammine chloride and cyanide by means of hydrogen (*Journ. Am. Chem. Soc.*, xxx., 1701). With the chloride, using different samples of material, two series of determinations were made, all weights being reduced to a vacuum.

Weight chloride.	Weight Pd.	Atomic weight.
0.89187	0.44885	106.40
0.77931	0.39218	106.38
0.66980	0.33711	106.41
1.08373	0.54541	106.40
0.96048	0.48338	106.40
Mean		106.399
0.95615	0.48129	106.43
0.94087	0.47356	106.42
0.90106	0.45353	106.42
1.16994	0.58908	106.50

Mean 106.442

Weight cyanide.	Weight Pd.	Atomic weight.
0.85860	0.47463	106.41
1.19378	0.66002	106.45
1.41818	0.78408	106.45
1.05254	0.58206	106.51
1.39510	0.77153	106.51
1.66196	0.91881	106.42

Mean 106.458

The mean of the fifteen determinations is $\text{Pd} = 106.434$, when $\text{Cl} = 35.473$, $\text{N} = 14.01$, and $\text{H} = 1.008$. Recalculation with $\text{Cl} = 35.46$ would lower this value slightly.

Uranium.—In two brief notes Oechsner de Coninck has given determinations of the molecular weight of uranous oxide, UO_2 (*Bull. Acad. Roy. Belg., Classe des Sciences*, 1907, 1041; 1908, [2], 163). First, by calcination of UO_2Br_2 to UO_2 he obtained values ranging from 271.19 to 274.09. Second, by reducing UO_2Cl_2 in hydrogen he found $\text{UO}_2 = 270.3$, 270.1, and 270.4. Figures of this character are evidently not entitled to serious consideration.

Columbium.—The atomic weight of columbium has been determined by Balke and Smith upon exceptionally pure material (*Journ. Am. Chem. Soc.*, xxx., 1644). The chloride, CbCl_5 , was decomposed by water with the aid of a little nitric acid, and the oxide so produced was finally ignited and weighed. The results, with vacuum weights, and with $\text{Cl} = 35.45$, are as follows:—

Weight CbCl_5 .	Weight Cb_2O_5 .	Atomic weight.
9.56379	4.71539	93.49
5.42242	2.65730	93.42
5.15992	2.54364	93.44
9.64854	4.75641	93.44
7.24572	3.57222	93.47
8.00559	3.94746	93.51
9.60763	4.73852	93.58
9.19732	4.53038	93.58

Mean 93.50

This value should supplant all the older determinations. With $\text{Cl} = 35.46$, $\text{Cb} = 93.54$.

Europium.—Jantsch (*Comptes Rendus*, cxlvi., 473) has re-determined the atomic weight of europium, by calcination of the octohydrated sulphate, using very pure material furnished by Urbain. The data are subjoined:—

Weight sulphate.	Weight oxide.	Atomic weight.
1.3501	0.6455	152.032
1.5054	0.7197	152.009
1.5213	0.7274	152.054
1.2881	0.6159	152.056

Mean 152.038

Calculated with $\text{H} = 1.008$ and $\text{S} = 32.06$.

Erbium.—Hofmann and Burger (*Ber.*, xli., 308), having at their command the original erbium material studied by Nilson and Krüss, subjected it to further purification, and determined the atomic weight of the "neo-erbium" so obtained. By conversion of the oxide into the sulphate they secured the subjoined data:—

Weight oxide.	Weight sulphate.	Atomic weight.
0.9048	1.4724	167.43
0.4666	0.7594	167.37
1.4181	2.3077	167.43
1.0789	1.7563	167.28

The highest value, 167.43, is preferred. Calculated with $\text{S} = 32.06$.

Ytterbium.—In my report for 1907, the work of Urbain upon ytterbium, by which it was decomposed into two elements, was mentioned. Urbain has since given a series of atomic weight determinations, made upon fractionated preparations of the old ytterbium, and these ranged regularly from 170.66 to 174.02 (*Comptes Rendus*, cxlvi., 406; see also *Chem. Zeitung*, xxxii., 730, a discussion of priority over Welsbach). The lower value is that of Urbain's "neo-ytterbium," the higher that of his "lutecium."

The same fractionation of ytterbium was also effected by Auer von Welsbach, who names the two new metals "cassiopeium" and "aldebaranium," respectively (*Monatsh. Chem.*, xxix., 181). By conversion of the oxides into the sulphates he obtained the following atomic weight data:—

Weight oxide.	Weight sulphate.	Atomic weight.
<i>Aldebaranium.</i>		
0.4181	0.6730	172.98
0.5984	0.9634	172.88
0.6173	0.9939	172.85
Mean		172.90
<i>Cassiopeium.</i>		
0.3716	0.5967	174.25
0.3086	0.4956	174.19
0.4026	0.6465	174.24
Mean		174.23

The nomenclature of Urbain has clear priority over that of Welsbach, and is therefore to be preferred.

Radium.—Three determinations of the atomic weight of radium, upon very pure material, have been made by Thorpe, who measured the ratio between RaCl_2 and 2AgCl (*Proc. Roy. Soc.*, A, lxxx., 298; *CHEMICAL NEWS*, xcvi., 229). His data are as follows:—

Weight RaCl_2 .	Weight AgCl .	Atomic weight.
0.0627	0.0604	226.8
0.0639	0.0618	225.7
0.0784	0.0753	227.7
Mean		226.7

Thorpe regards the atomic weight as now known to within a unit, and notes the agreement between his work and that of M^{me}. Curie. In order to check his method of determination, which involved the use of very small quantities of material, he made similar analyses of barium chloride and bromide, and obtained results in accord with those of Richards.

(NOTE.—H. Wilde has argued on theoretical grounds, that $\text{Ra} = 184$. See *Mem. Manchester Lit. Phil. Soc.*, No. 1, 1908, and *Phil. Mag.*, [6], xv., 280, and xvi., 825).

Krypton and Xenon.—Moore, from the residues from 120 tons of liquid air, has isolated krypton and xenon in considerable quantities (*Proc. Chem. Soc.*, xxiv., 273). The densities, referred to $\text{O} = 16$, and the corresponding atomic weights were as follows:—

	Kr.	Xe.
Density	41.506	65.35
Atomic weight . .	83.012	130.70

In this connection it may be stated that Boltwood assigns to his "ionium" an atomic weight of about 230 (*Am. Journ. Sci.*, [4], xxv., 380).

(NOTE.—A. T. Cameron, in *Science Progress*, ii., 525, has given estimates of probable atomic weight for a number of radio-active emanations).

Miscellaneous Notes.

The subject of atomic weights in general has been treated by several authors. There is a useful summary by Richards, of the Harvard work (*Journ. Chim. Phys.*, vi., 92), and an essay by Lemoine on the unity of matter and the determination of atomic weights (*Rev. des Questions Scientifiques Bruxelles*, [3], xiv., 182). Also a lecture by Jaqueroed on modern researches upon atomic weights (*Rev. Gén. des Sciences*, xix., 443). Comstock has discussed the variability of these constants (*Phil. Mag.*, [6], xv., 12), and the evolution and devolution of the elements is considered by A. C. and A. E. Jessup (*Phil. Mag.*, [6], xv., 21). Bernoulli has attempted to compute the atomic weights on purely theoretical grounds (*Phys. Zeit.*, ix., 745), and so too has Stevens ("The Massing of Spheres," London, 1908; privately published).

On the calculation of atomic weights there are papers by Noyes (*Journ. Am. Chem. Soc.*, xxx., 4), Hinrichs (*Chem. Zeit.*, 1908, [1], 1240; *Comptes Rendus*, cxlvi., 971; cxlvii., 797 and 1302), Dubreuil (*Comptes Rendus*, cxlvii.,

627, 856, and 1300), and Leduc (*Comptes Rendus*, cxlvii., 972). The electro-chemical equivalents of oxygen and hydrogen have been studied by Lehfeldt (*Phil. Mag.*, [6], xv., 614). On the silver voltameter and coulometer there are elaborate papers by Duschak and Hulett (*Trans. Am. Electrochem. Soc.*, xii., 257), and by Smith, Mather, and Lowry (*Phil. Trans.*, A, ccvii., 545). In the latter research the electro-chemical equivalent of silver is fixed at 1.11827 mgrm. per coulomb.

In the International Table, published in the *Journal of the American Chemical Society* for March, there is a serious misprint. Zn should be 65.37 instead of 65.7.—*Journal of the American Chemical Society*, xxxi., No. 3.

THE USE OF BAKELITE FOR ELECTRICAL AND ELECTRO-CHEMICAL PURPOSES.*

By L. H. BAEKELAND, Sc.D.

(Concluded from p. 19).

Moulding Processes.—The simplest but slowest way for moulding Bakelite is to pour liquid A, alone or mixed with fillers, in suitable moulds and heat in a Bakeliser. This operation may take as much as one to three hours, according to the temperature or the size of the object; so that this process has the objection of requiring the relatively long use of moulds. It can be shortened by simply carrying the heating process until the B stage, after which the objects can be expelled from the moulds and finished in the Bakeliser at any suitable time thereafter and without the further use of moulds. The B stage can be obtained by plain but slow heating in a stove or water-bath, or by rapid heating in the Bakeliser. But even all this is too slow for many purposes where quick and accurate moulding is essential. It then becomes simpler to mould in a hot press. For this purpose a hydraulic press, or a screw press, or even a lever press can be used, as long as it is provided with contrivances whereby the plateens can be heated and cooled quickly, either by steam and cold water circulation, or by gas heating. Temperatures as high as 200° C. are desirable for rapid and best work, but the moulding can be done also at 80 lbs. steam pressure. It is a noteworthy fact that moulds under high pressure contact with the plateen, heat up and cool quicker than if not under pressure.

I tried first mixtures of liquid A with various filling materials, the mass being mixed between rollers same as are used in the rubber industry, but I found afterwards that this slow and expensive method of mixing is entirely necessary if solid A be used.

Furthermore, liquid A has the disadvantage over solid A of requiring a longer time for moulding. Solid A has the great advantage over other plastics in that the first action of heat liquefies it entirely, so that high pressures as required for moulding celluloid, rubber, or resinous materials are superfluous unless large amounts of filling materials be used which make the mass less plastic. After the first liquefying action of the heat, the immediate after-effect is quite contrary; namely, the hardening of the mass while A becomes B, then C. The main function of the pressure in the act of moulding A is to counteract the dissociation which would cause porosity and resulting lack of homogeneity. This explains why astonishingly accurate moulding—for instance, talking machine records—can be made with Bakelite under low pressure, provided sufficient heat be used. Persons who are familiar with the moulding of celluloid, shellac, or rubber compositions, when trying Bakelite for the first time, are apt to heat the moulds insufficiently, being under the wrong impression that high temperatures may spoil Bakelite in the same way as the compounds to which they are accustomed.

* A Paper presented at the Fifteenth General Meeting of the American Electro-chemical Society at Niagara Falls, Canada, May 6th to 8th, 1909.

Electrical Tests.			
No.	Name of piece.	Bakelite.	Remarks.
1.	Spool.	Punctured at 16,000 to 18,000 volts.	Asbestos hard - rubber composition punctured at 4000 to 8000 volts.
2.	Square tube (hollow); thickness, 0.103 inch.	Punctured at 21,000 volts.	Asbestos hard - rubber composition punctured at 17,000 volts.
3.	Washer; thickness, 0.062 in.	Punctured at 20,000 volts.	Asbestos hard - rubber composition punctured at 11,000 volts.
4.	Discs of various compositions. Thickness, 0.0625 inch.	Punctured at 45,000 volts.	These tests are still unfinished, and were made on various Bakelite compositions. None on pure Bakelite.
	" 0.162 "	" 31,000 "	
	" 0.165 "	" 22,000 "	
	" 0.375 "	" 42,000 "	
5.	Disc; thickness, 0.095 inch.	" 18,000 "	Asbestos hard - rubber composition punctured at 1500 volts.
6.	Cup insulator; thickness, 0.375 inch.	" 42,500 "	
7.	Line insulator.	Arc to pin, dry at 50,000 volts.	Used on 11,500 volt line.
8.	Rail insulator.	Resistance (dry), 5625 megohms. Resistance (wet), 0.5 to 65 megohms. (These tests are only approximate in megohms). Arc over hook bolt to rail, 27,000 volts.	Porcelain resistance: Dry, 4550 megohms. Wet, 0.2 to 10 megohms. Porcelain arc over 26,400 volts.
Mechanical Strength Tests.			
2.	Square tube (hollow); thickness, 0.103 inch.	Traverse strength, 6-inch centres, 1850 pounds.	Asbestos hard - rubber composition 1700 pounds.
8.	Rail insulator.	Ultimate strength compression, 96,000 to 110,000 pounds. Ultimate strength tension, 3200 to 5500 pounds. Impact test: no limit found for same blow as porcelain was submitted to.	Porcelain, 45,000 to 85,000 pounds. Porcelain, 1400 to 2300 pounds. Porcelain 38 to 100 blows.
9.	Cup piece; hollow cylinder, 3 ins. high, 1½ ins. diameter, 0.045 in. thick.	Ultimate compressive strength, 2550.	Loaded on top.
Heat Tests.			
10.	Valve interior.	At 265 pounds, steam about 460° F. for one hour.	No effect on the composition.
11.	Packing nut; graphite composition.	Tight at 65 pounds, steam 200 r.p.m.	Could turn 3-inch shaft by hand.

NOTE.—All of the Bakelite insulation shows an unusual uniform resistance at varying temperatures from 0° to 300° C., and does not soften at much higher temperatures. Most of the insulation contained about one-third Bakelite and two-thirds finely-divided asbestos.

The great penetrating power of A makes it possible to making moulded objects containing as little as 10 per cent and even less of Bakelite, the remainder being made up of suitable fillers, for instance, asbestos.

Quantities of 20 to 30 per cent of solid A and 80 to 70 per cent of asbestos make excellent compositions for moulded insulators.

In some cases it may be found desirable to increase the amount to about 40 per cent. Wood pulp or ground sawdust require these larger proportions if the objects have to stand boiling water without losing their gloss.

The mixing of these compounds is very simple work. The solid A is pulverised in a porcelain ball mill and ground to 50 or 100 mesh. If trouble is experienced on account

of the ground material sticking to the walls of the mill, this can be easily obviated by adding about 10 per cent of the filler, which prevents "caking." The so ground A can be kept in reserve for further use. It is then mixed in suitable proportions with the finely powdered filling materials and re-ground in a ball mill so as to insure thorough mixing. This mixed powder is now ready for moulding; on account of its bulkiness it may be found preferable to compact it somewhat by pressing it slightly or rolling it into sheets while being gently heated. The resulting sheets or cakes can be kept in stock. To use these for moulding they are put into the slightly heated moulds, and the latter are pressed now between the very hot platens of the press, which squirts out any excess of

material. Pressing and heating is continued until the A is transformed into B, after which the moulds can be emptied. According to the size of the moulded objects or the temperature, moulding is finished in a time varying from twenty-five minutes to three minutes, and even less for small objects.

Moulded objects of Bakelite in B condition are about as strong as shellac, but they still soften under the influence of heat. They become considerably stronger and acquire their final resisting qualities by being heated in the Bakeliser. This final treatment can be carried out at any suitable time, all the pieces being put in together. No moulds are needed here because B, although soft while hot, does not melt any longer, and keeps its shape while submitted to the high heat of the Bakeliser.

We here observe again a slight shrinkage of volume, which has to be taken into consideration while designing the moulds. This contraction is always the same for the same compositions, and becomes very small if large amounts of fillers are used. By taking these factors into consideration the moulding can be done with an accuracy of 0.001 inch or better.

We have stated above that C can not be moulded; it is no longer a plastic; in other terms its particles if pressed together do not give a strong coherent mass where all the particles are welded homogeneously together.

On the other hand, B, although infusible and insoluble, softens when heated under high pressure, and welds and moulds together.

This enables us to still further simplify the moulding operation by using ground B instead of A. But it then becomes necessary to use maximum temperatures and highest possible pressure, B not flowing so easily as A. This is specially indispensable when large amounts of filling material are employed. This method of working is decidedly advantageous when a highly polished surface and very accurate moulding is desired. By keeping long enough in the mould, no after-treatment in the Bakeliser is required, and the gloss imparted by a polished mould is thus kept intact. The use of B is also advisable in such instances where mixtures rich in Bakelite are desired. Whenever mixtures are made containing over 40 or 50 per cent of A there is constant danger that during the act of moulding the A may ooze out before it has had time to be changed into B. By using directly B this difficulty no longer exists, and there is no further limit to the quantities which may be employed in a moulding mixture.

For such moulded electric insulators which are expected to stand high temperatures, finely ground asbestos, clay, mica, or other similar mineral fillers should be used. If temperature specifications are not so important, then organic fillers like wood-pulp or ground sawdust are available, and give nicely moulding compositions of which the insulating coefficient is frequently considerably higher than that of asbestos. Some varieties of Canadian asbestos prove to be much less desirable for high voltage insulation; this is probably due to mineral impurities and to the higher content in water. These differences in insulating properties do not play much importance for voltages below 40,000. On the other hand, asbestos, on account of its fibrous texture, lends great strength to Bakelite compositions and makes them stand better the shattering effect of direct impact or concussion.

The difference in insulating properties of asbestos is clearly shown by comparing results with a sheet of blotting paper impregnated with Bakelite and of asbestos paper of the same thickness, treated in the same way. The impregnated blotting paper may puncture at voltages two and three times higher than the asbestos sheet.

Bakelite compositions lend themselves more or less to kneading, filing, and sawing, according to the nature of the filler. In this direction, compositions containing fibrous materials show again the best results.

I have stated before that Bakelite alone can stand 300° C., but compounds which contain large amounts of mineral filler may be made to stand even higher temperatures.

Those containing wood pulp, sawdust, or other organic fillers will stand less, the filling material being destroyed before Bakelite.

It is a well known fact that whenever rubber is used as an insulator it slowly emits sulphur vapours, which by and by attack metallic parts and may cause serious injury to delicate copper wires or metallic connections. Bakelite, not emitting any such objectionable emanations, does not possess this defect, and therefore has been preferred in the manufacture of delicate electrical instruments.

But I have not yet mentioned another advantage of Bakelite insulators over those made of shellac or other resinous materials.

It is a known chemical fact that the latter are all apt to hydrolyse by the action of water or dilute alkalis. This action is readily shown whenever water is dripped on a table varnished with shellac, which causes whitening on the wet spots. This effect is more pronounced whenever a small amount of ammonia is present. A similar action occurs whenever the conditions of the atmosphere deposit a thin film of moisture on shellac insulators, so much the more as the air always contains traces of ammonia. This superficial hydrolysis which forms on the surface of resinous insulators a thin film of conductive, chemically changed resin, may explain the so-called "creeping" of high voltage currents along the surface of resinous insulators. The very fact that Bakelite can be heated in presence of water and ammonia in an autoclave at 200° and over without hydrolysis makes us feel safe as to its resisting power to atmospheric influences.

Whether Bakelite-asbestos or Bakelite-mica insulators will answer the purpose for high voltage insulation as well or worse than porcelain is a matter which experience and the test of time alone can decide.

For insulation in third-rail systems, where continuous vibration of passing trains plays havoc with brittle and unreliable porcelain, Bakelite-asbestos has indicated decided superiority after several months of continuous service, as well as by direct laboratory tests; besides greater strength, it has shown more regularity in manufacture and allows more accurate moulding, which permits closer designs and smaller margin of safety.

There is no difficulty whatever in imbedding metallic parts, like bolts, cores, screws, washers, or reinforcing members, in the moulded brass.

In the accompanying table are condensed some comparative results which have been communicated to me by users of Bakelite who previously had acquired great skill in the manufacture of other excellent insulating compounds, and by this fact were better able to draw comparisons.

Before leaving this subject mention should be made of the properties of special mixture of Bakelite with graphite, of which I have here some specimens. Both these materials compounds very well together in almost any proportions. Liquid A or solid A can be used for this purpose. By varying the amounts of Bakelite, these compositions may be made of varying hardness from such ones as write on paper like the softest pencils, to others which are so hard that they no longer leave a tracing when rubbed against a rugous surface. I do not know in how far this may be utilised in the pencil industry, but I have obtained some very encouraging results by trying to use them for self-lubricating bearings. The fact that such bearings can be moulded very accurately at little cost makes their interchangeability and rapid renewal a very easy matter. Dynamos or motors or other rapid revolving machinery where lubrication is a delicate matter, might be provided with such bearings instead of the older metallic bearings. Bakelite-graphite bearings will not melt nor soften in case of overheating; they can be used in conjunction with oil like any other bearing, and in case of insufficient supply of oil the graphite present will supply the necessary lubricant.

As a lining for pumps which are required to handle liquids which corrode iron, the same mass may find its uses.

But Bakelite-graphite composition presents other possibilities from an electrical standpoint. It namely gives us a means of producing a material of which the electrical resistance can be changed at will in a very wide range by changing the proportion of Bakelite.

Finally, I might mention that I have tried to decrease the porosity of graphite anodes in electrolytic cells by the injection of extra thin liquid A, and Bakelising afterwards; but although in a first experiment we were able to decidedly decrease anode corrosion, I am not yet sure whether this was due to direct action or to a somewhat lessened conductivity. This may be a suggestion for Dr. Turrentine in his experiments with graphite as electrodes for electrolytic analysis.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, June 17th, 1909.

Prof. HAROLD B. DIXON, F.R.S., President, in the Chair.

(Concluded from p. 23).

171. "The Oxidation of Hydroxy-derivatives of Benzaldehyde and Acetophenone." By HENRY DRYSDALE DAKIN.

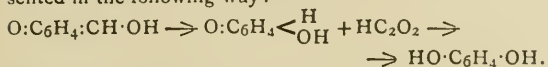
Ortho- and para-hydroxybenzaldehydes, when warmed with ammonia and hydrogen peroxide, readily give good yields of catechol and quinol respectively. Similarly, *o*- and *p*-hydroxyacetophenones yield the same products. The amount of hydroxybenzoic acid formed in both cases is quite insignificant. The corresponding *m*-hydroxy-derivatives, on similar treatment, undergo normal oxidation, and yield *m*-hydroxybenzoic acid.

A number of other *o*- and *p*-hydroxy-derivatives were found to behave similarly on oxidation. 5-Nitro-2-hydroxybenzaldehyde gives nitrocatechol, and 4-hydroxy-3-methylbenzaldehyde, and 2-hydroxy-4-methoxyacetophenone yield 2-methoxyquinol, and 4-methoxyquinol respectively. Resacetophenone and 2:5-dihydroxyacetophenone probably react in the same manner, but the resulting trihydric phenols are too unstable in alkaline solution to be easily isolated.

If the hydroxyl group in the *o*- or *p*-hydroxybenzaldehyde and hydroxyacetophenone be replaced by a methoxy-, ethoxy-, nitro-, or amino-group, no formation of a phenol occurs, but usually a small yield of the corresponding benzoic acid is obtained.

A large number of methoxy-, ethoxy-, nitro-, and amino-derivatives of benzaldehyde and acetophenone, which did not contain a free hydroxy-group in the *o*- or *p*-position, were all found to yield the corresponding benzoic acids on oxidation. The yields were usually small, as these substances are much more resistant to the action of hydrogen peroxide than the *o*- and *p*-hydroxy-derivatives. The above results may be explained on the assumption that the salts of *o*- and *p*-hydroxybenzaldehydes and the *o*- and *p*-hydroxyacetophenones possess a quinonoid structure, as already suggested by Hantzsch in the case of some of the salts of *o*-hydroxybenzaldehyde (*Ber.*, 1906, xxxix., 3081), and it also furnishes an explanation of the different behaviour on oxidation of the corresponding *m*-compounds, which presumably do not possess this structure.

The oxidation of *p*-hydroxybenzaldehyde may be represented in the following way:—



172. "The Intramolecular re-arrangement of Diphenylamine Orthosulphoxides." By EDWARD DE BARRY BARNETT and SAMUEL SMILES.

It was shown that the orthosulphoxides of diphenylamine are converted by the action of certain acid reagents

into the orthoquinonoid derivatives of phenazothionium. The reaction has been studied with the tetranitro-, di-*p*-nitro-, isodinitro-, and the unsubstituted sulphoxide, and it has been found that the change proceeds the more readily the stronger the basic properties of the quadrivalent sulphur. The last-named sulphoxide furnishes phenazothionium chloride.

173. "Double and Triple Ferrocyanides of Magnesium, Aluminium, and Cerium with Potassium and Ammonium." By FREDERIC WILLIAM ROBINSON.

The author has investigated the above salts in order to ascertain whether the triple salts are definite compounds or amorphous mixtures of double salts.

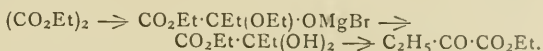
Magnesium.—Salts of the composition $\text{R}_2\text{MgFeC}_6\text{N}_6$ (R being the alkali metal) have been obtained and their properties investigated. Salts of varying composition $\text{RR}_1\text{MgFeC}_6\text{N}_6$, were produced under different conditions, the ratio R/R_1 varying according to the conditions of preparation.

Aluminium.—Salts of the composition $\text{RAlFeC}_6\text{N}_6\cdot\frac{1}{2}\text{H}_2\text{O}$ were isolated, which, when dehydrated, are very similar to Prussian blue. A series of triple salts, $[\text{NH}_4\cdot\text{K}]\text{AlFeC}_6\text{N}_6$, was prepared, and when the alkali metal was in large excess, salts were obtained containing two equivalents of the alkali metal and two of aluminium per unit of acid radicle.

Cerium.—Crystalline double salts have been obtained possessing the composition $\text{RCeFeC}_6\text{N}_6$. They exhibit very similar phenomena both in their formation and properties to the analogous aluminium salts. The constitution of the triple cerium potassium ammonium salts has also been established.

174. "Action of Grignard's Reagent on Ethyl Oxalate." By JOHN KENNETH HAROLD INGLIS and ALFRED SIDELL MASON.

In the hope of finding a convenient method of obtaining α -ketonic acids, the above action has been investigated. It was supposed that by acting on the ester with magnesium ethyl halide the hydrolysis of the resulting additive product would yield propionylformic acid according to the following scheme:—



Magnesium ethyl bromide was therefore allowed to react with the dry ester in molecular proportions. After hydrolysis of the resulting mixture with dilute sulphuric acid and ice, the ethereal solution was dried and fractionally distilled under 25 mm. pressure. The acid boils at $74\text{--}78^\circ/25\text{ mm.}$, and the ester at $74\text{--}77^\circ/25\text{ mm.}$ Between 74° and 83° 12.5 grms. of a pale yellow liquid were obtained, the theoretical yield for the ester being 65 grms. This liquid appeared to be a mixture of ester and acid. The oxime of the acid melted sharply at 154° , the melting-point of α -oximinobutyric acid.

Similar experiments were carried out with magnesium phenyl bromide in the expectation of obtaining phenylglyoxylic ester. This ester boils at $151\text{--}154^\circ/30\text{--}40\text{ mm.}$, and 18 grms. of a yellow oil were obtained boiling between 140° and 160° , the theoretical amount being 89 grms. The phenylhydrazone of the acid was prepared and found to contain 11.86 per cent of nitrogen (theoretical, 11.66); after re-crystallisation from alcohol it melted at 147° . The attempt to isolate the acid was, however, unsuccessful.

The above results point to the possibility of preparing these two esters from oxalic ester. It is hoped to continue these experiments with a view to ascertain the conditions under which the yield may be increased.

175. "The partial Racemism of Menthyl *r*-Mandelate." By ALEXANDER FINDLAY and EVELYN MARION HICKMANS.

From a study of the solubility relations at 35° , 25° , 10° , and 0° , it has been found that *l*-menthyl *r*-mandelate is stable at these temperatures, and from a crystallisation experiment at -15° , it would appear that even at this temperature the transition-point has not been reached, so

that resolution of *r*-mandelic acid by crystallisation of its *l*-menthyl ester cannot be effected at temperatures above -15° . The transition-point must lie below this, and has not been determined.

176. "The Primary Interaction of Chlorine with Acyl-anilides." By KENNEDY JOSEPH PREVITÉ ORTON and WILLIAM JACOB JONES.

It has been shown, by measuring the free chlorine in the solution, that chlorine and acylanilides (or chloroamines and hydrochloric acid) in acetic acid solution enter into a reversible reaction, which is represented by the equation $\text{Ar}\cdot\text{NHAc} + \text{Cl}_2 \rightleftharpoons \text{Ar}\cdot\text{NClAc} + \text{HCl}$. Equilibrium is attained extremely rapidly, but is gradually disturbed by the chlorination of the anilide (when that is possible) which follows slowly on the primary reaction.

The following table gives the extent of the reaction in various cases when the anilide and the chlorine are respectively, in the first instance, at a concentration of 0.025 grm.-molecule per litre:—

Anilide.	Percentage of chlorine combined in—		
	75 per cent acetic acid.	50 per cent acetic acid.	Glacial acetic acid.
(<i>p</i>) $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}$..	39.5	11	0
(2:4) $\text{Cl}_2\cdot\text{C}_6\text{H}_3\cdot\text{NHAc}$..	80	34	0
(2:4) $\text{Cl}_2\cdot\text{C}_6\text{H}_3\cdot\text{NH}\cdot\text{CHO}$	83.5	32	0
(2:4) $\text{Cl}_2\cdot\text{C}_6\text{H}_3\cdot\text{NHBz}$..	62	14	0
(<i>s</i>) $\text{Br}_3\cdot\text{C}_6\text{H}_2\cdot\text{NHAc}$..	86	43	0

The measurements in 50 per cent acetic acid lead to an equilibrium constant, but in 75 per cent no constant can be calculated. In 65 per cent acetic acid, a constant is obtained if the reaction is represented as $\text{Ar}\cdot\text{NHAc} + \text{Cl}_2 \rightleftharpoons \text{Ar}\cdot\text{NClAc} + \text{H}\cdot + \text{Cl}'$; that is, the equilibrium constant is proportional to the square of the concentration of the hydrochloric acid.

It will be seen that the primary reaction between the anilide and the chlorine does not occur to a measurable extent in glacial acetic acid; nevertheless, in the presence of a molecular proportion of sodium acetate, more than 90 per cent of the chlorine reacts. In 50 per cent acetic acid, on the other hand, there was only a trace of free chlorine.

The method of estimating the free chlorine, which requires only two to three minutes, consists in the aspiration of a small volume of air through the solution, such that about 5 per cent of the free chlorine is extracted. Comparison with experiments made with standard solutions of chlorine gives the measure of free chlorine. With the apparatus which the authors have elaborated, the measurements can be made with a high degree of accuracy, the differences in the value of the free chlorine in two similar experiments never exceeding 0.05 cc. of N/10 thiosulphate.

177. "The Quantitative Decomposition of the Anilides: a Study in Steric Influence." By OLIVER CHARLES MINTY DAVIS.

A series of experiments have been carried out on the quantitative hydrolysis of the anilides by means of sodium hydroxide.

The object of the research was to investigate the effect of orientation in the selected compounds on their chemical reactivity.

A considerable number of anilides were experimented on, and the main result of the work is to show that under the conditions chosen by the author the chief effect of substituent elements and groups (and their position in the molecule) is to influence the rate of decomposition.

178. "Note on the Anomalous Viscosity of Nitrobenzene." By FERDINAND BERNARD THOLE.

In support of his theory of "motosomerism" (*Ber.*, 1907, xl., 508), Knoevenagel quoted the results obtained by Mühlenbein with regard to the viscosity of nitrobenzene.

Mühlenbein (*Diss.*, Cöthen, 1901) stated that the viscosity of freshly distilled nitrobenzene decreased by 0.7 per cent on standing for some hours. This he attributed to a change in the configuration of the nitro-group. He also

drew attention to the fact that specimens of quinoline derived from various sources possess widely different densities and viscosities. The boiling-points of the specimens used, however, seemed to show that these were by no means sufficiently pure to give trustworthy physical constants.

Repetition of Mühlenbein's work on nitrobenzene does not confirm his results.

The mean results of four series of observations using nitrobenzene from various sources are as follows:—

	Immediately after distillation.	After 22 hours.
Mean density ($25^{\circ}/4^{\circ}$) ..	1.19370	1.19869
Mean viscosity (25° C.) ..	0.018226	0.018224

The mean difference in viscosity, namely, 0.0012 per cent, is well within the limits of experimental error.

The carefully purified quinoline used (b. p. 235°) had a density of 1.08994 and a viscosity of 0.033724. Mühlenbein obtained densities varying between 1.08228 and 1.09351, and viscosities between 0.033911 and 0.045405.

The Viscosity of Ethyl Acetoacetate.—Schaum (*Ber.*, 1898, xxxi., 1964) and Dunstan and Stubbs (*Trans.*, 1908, xciii., 1919) have pointed out that the physical constants of freshly distilled ethyl acetoacetate change on keeping the ester for some time. A closer study of this change has been carried out, and curves have been plotted showing the change of viscosity and density with time.

The viscosity and density are found to increase rapidly at first, and then more slowly, until equilibrium is attained. Extrapolation gives a density of, approximately, 1.02045 and a viscosity of 0.015210 for the ester immediately after distillation.

The low initial viscosity shows that the freshly distilled liquid exists almost entirely in the ketonic form.

179. "Studies of the Carbonates. Part I. The Equilibrium between Calcium Carbonate and Carbonic Acid." By CLARENCE ARTHUR SEYLER and PERCY VIVIAN LLOYD.

Schlössing's law has been verified by means of double titration with methyl-orange and phenolphthalein as indicators.

The following general law has been established in the case of waters containing calcium chloride and sulphate, sodium bicarbonate, chloride, and sulphate, and magnesium sulphate in quantities such as occur in fresh natural waters. "When a water is in equilibrium with the limestone which it percolates, the square of the alkalinity is directly proportional to the free carbonic acid and inversely to the total hardness." The alkalinity and hardness being expressed in grm.-equivalents per litre, and corrected for degree of ionisation, the constant has the value $F \pm 10^{-4}$, where F is on the average 113.

The constant F is called the "saturation factor" of the water, and is a criterion as to whether the water is saturated or not with the limestone.

For mineral water or sea-water the factor would be higher.

For different forms of calcium carbonate (calcite and arragonite) the factor F is proportional to the "solubility product" and to the square of the solubility in pure water.

180. "Some Esters of Arsenious Acid. Part II. Resorcinylyl Arsenite." By WILLIAM ROBERT LANG and JOHN OBINS WOODHOUSE.

Continuing the experiments described in a previous communication (Lang, MacKey, and Gortner, *Trans.*, 1908, xciii., 1364), but using one of the dihydric phenols, quantities by weight of resorcinol and of arsenious oxide corresponding with the equation below were heated to the melting-point of the former in a distilling flask, connected through a weighed flask with an exhaust pump. The temperature was kept constant, and the arsenic slowly dissolved in the melted resorcinol, yielding an amber-coloured fluid becoming darker as the heating progressed, the pressure being 60 mm. The water evolved in the reaction, $3\text{C}_6\text{H}_4(\text{OH})_2 + \text{As}_2\text{O}_3 = (\text{C}_6\text{H}_4\text{O}_2)_3\text{As}_2 + 3\text{H}_2\text{O}$, collected in

the trap, and was weighed as a check, due precautions being taken to prevent loss. After heating for fifty-five minutes the mixture was allowed to cool, broken up, and extracted with hot toluene, which removed from it some resorcinol. The residue was dissolved in dry ethyl alcohol, in which these esters are soluble, when an immediate precipitate of arsenious oxide was produced. Analysis of the substance obtained on evaporation in a vacuum of the alcoholic extract proved it to contain from 5 to 6 per cent of arsenious oxide in excess of that required by the formula $(C_6H_4O_2)_3As_2$, showing that arsenious oxide dissolved in the ester formed. To prevent this, an excess of resorcinol was employed, namely, 100 grms., and 50 grms. of arsenious oxide heated with it as before, the proportions of the former to the latter being, according to the equation supposed to represent the reaction, 100 to 60; in this way an amount of resorcinol corresponding with 10 grms. of arsenious oxide would, of necessity, remain unacted on and be readily extracted from the ester by a specific solvent. After an hour's heating, the solidified mass was broken up and digested in a reflux condenser with dry toluene, which extracted a considerable proportion of resorcinol. This treatment was repeated until no more resorcinol could be obtained on evaporation of the solvent. The resorcinol-free mass was analysed as follows:—About 1 grm. was treated with water, which caused its immediate decomposition, the solution acidified with hydrochloric acid, and the arsenic precipitated as sulphide, dried on a tared filter, and weighed. The results of numerous analyses, which closely corresponded, gave:—

Found, As = 31.9; $C_{18}H_{12}O_6As_2$ requires As = 31.65 per cent.

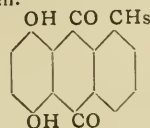
Resorciny arsenite closely resembles hardened gelatin in appearance, melts at 24° , and has a specific gravity of 1.9. It is soluble in methyl, ethyl, propyl, and butyl alcohols, but insoluble in ether, chloroform, benzene, or toluene. Water, however, immediately decomposes it.

The same experiments were tried with quinol, but, so far, without success.

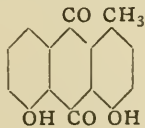
181. "The Constitution of Chrysophanic Acid and of Emodin." (Preliminary Note). By FRANK TUTIN and HUBERT WILLIAM BENTLEY CLEWER.

It was considered highly probable by Jowett and Potter (*Trans.*, 1903, lxxxi., 1327) that chrysophanic acid is represented by Formula I., and that emodin differed from this compound by the presence of one additional hydroxyl group.

By a comparison of the properties of quinizarin and 2-methylquinizarin respectively with those of chrysophanic acid, the present authors have obtained conclusive proof that the last-mentioned compound does not contain the quinol grouping. There is reason to believe, furthermore, that chrysophanic acid is represented by Formula II.; that is to say, that it is 1-methylchrysazin. Emodin will then be, in all probability, a hydroxy-1-methylchrysazin, but the position of the additional hydroxyl group is at present uncertain.



I.



II.

The work is being continued, and it is hoped to obtain further evidence in support of the above conclusions, which, if they are correct, indicate that chrysophanic acid is very closely related to both aloë-emodin and rhein (compare Robinson and Simonsen, *Proc.*, 1909, xxvi., 76).

182. "The Morphotropic Relationships between the Derivatives of Picric Acid." By GEORGE JESUSALEM.

The author has prepared a number of salts of picric and styphnic acids with primary, secondary, and tertiary amines and quaternary ammonium bases, and has determined their

crystallographic constants. The discussion of the data thus obtained shows that the crystalline forms of these substances all fall into the scheme devised by Barlow and Pope; a considerable amount of quantitative confirmation of the correctness of the structure assigned to benzene by these authors has thus been collected.

The author further shows that the molecular volumes of the salts in question are directly proportional, within limits of + or - 4 per cent, to the sums of the valencies composing the molecular complexes. Further confirmation is thus provided of the conclusion that each atom in a compound substance appropriates a portion of the total volume directly proportional to its fundamental valency.

183. "A possible Intramolecular Change in the Inactive Phenylalkoxyacetic Acids." (Preliminary Note). By WILLIAM ERNEST STEPHEN TURNER.

Attention has already been drawn to the steady decrease occurring, as dilution proceeds, in the values of the dissociation constants of phenyl-methoxy-, -ethoxy-, and -propoxy-acetic acids (Findlay, Turner, and Owen, *Trans.*, 1909, xcv., 939).

The author has found that aqueous solutions of phenyl-propoxyacetic acid become yellow on keeping for a long period, and deposit a yellow solid from which, by means of ether, pale yellow needle-shaped crystals, m. p. 144° , have been obtained. Moreover, in the liquid state, carefully purified samples of the ethoxy- and propoxy-acids deposit yellow needles at a very slow rate.

The crystals isolated from the liquid propoxy-acid consist of two substances, the main constituent melting at 152° . Physico-chemical experiments show that whereas these crystals have the same molecular weight as phenylpropoxyacetic acid, they differ from it in constitution.

Owing to the slow rate at which it proceeds, and the consequent difficulty of accumulating materials, the exact nature of the change occurring cannot yet be determined.

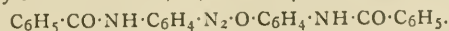
184. "The Colour and Constitution of Diazonium Salts." (Part I.). By GILBERT T. MORGAN and MARY ALCOCK.

The diazonium salts of benzoyl-1:4-naphthylenediamine, which are stable coloured substances, have now been compared with the corresponding derivatives of benzoyl-*p*-phenylenediamine and its alkylated homologues.

Benzoyl-p-aminobenzenediazonium chloride and the corresponding nitrate, sulphate, perchlorate, and acetate are also remarkably stable, but colourless when freshly prepared. *as-Benzoylmethyl-p-phenylenediamine* and *as-Benzoylethyl-p-phenylenediamine*, colourless needles, m. p. 153° – 154° and 117° respectively, give rise to colourless only diazonium salts with the commoner mineral acids; their diazonium molybdates and tungstates are, however, solid and colourless.

The conclusion is drawn that the absence of colour in the diazonium salts of benzoyl-*p*-phenylenediamine and its homologues, and the presence of colour in the corresponding series of diazo-derivatives from benzoyl-1:4-naphthylenediamine, is dependent on the differences between the chromogenic properties of the benzene and naphthylene nuclei respectively, rather than to any variation in the structure of the diazonium complex contained in the colour salts derived from the naphthalene base.

The foregoing diazonium salts couple with the undiazotised base in the usual way to form diazoamines, such as the compound $C_6H_5 \cdot CO \cdot NH \cdot C_6H_4 \cdot N_2 \cdot NH \cdot C_6H_4 \cdot NH \cdot CO \cdot C_6H_5$, but when treated with aqueous sodium hydroxide or ammonia they lose a portion of the diazo-nitrogen, and yield diazo-oxides, as, for example,—



185. "The Hydrolysis of Amygdalin by Acids." (Part I.). By JAMES WALLACE WALKER and VERNON K. KRIEBLE.

A comparative examination has been made of the action of dilute and concentrated hydrochloric and sulphuric acids, as well as of concentrated aqueous oxalic and trichloroacetic acids on amygdalin. It is found that, whilst con-

centrated hydrochloric acid first attacks the nitrile radicle, producing *l*-amygdalinic acid, a solution of sulphuric acid of corresponding strength liberates *l*-mandelonitrile. Oxalic acid behaves in a manner similar to dilute hydrochloric, but trichloroacetic acid does not hydrolyse amygdalin at all under the same conditions of temperature and concentration at which hydrochloric acid readily effects the hydrolysis.

186. "Some Derivatives of Anthraquinone." By DOROTHY HARROP, ROLAND VICTOR NORRIS, and CHARLES WEIZMANN.

The authors have prepared a number of derivatives of 1:2-, 1:3-, and 1:4-dimethylanthraquinone. By the action of sulphuric and boric acids on the dichlorodimethylbenzoylbenzoic acids produced by condensing 1:4-dichlorophthalic anhydride with the three xylenes in presence of aluminium chloride, the corresponding dichlorodimethylanthraquinones are obtained. The chlorine atoms in the latter compounds are easily displaced, and the corresponding dianilino-, diphenoxy-, and dithiophenoxyl-derivatives have been isolated.

The following note has been received since the meeting:

187. "Isomeric Derivatives of Phosphoric Acids." By FREDERIC STANLEY KIPPING and BERNARD DUNSTAN WILKINSON LUFF.

Many salts prepared by combining phenyl-*p*-tolylphosphoric acid, PO(OPh)(O·C₆H₄Me)·OH, with an optically active base have been examined, but so far all attempts to resolve the acid have been unsuccessful. Nevertheless, evidence that the acid is a mixture of isomerides has been obtained by treating phenyl-*p*-tolylphosphoric chloride with asymmetric bases (compare Kipping and Hall, *Trans.*, 1901, lxxix., 442). With *dl*-hydrindamine, for example, the chloride yields a mixture of two isomeric hydrindamides, PO(OPh)(O·C₆H₄Me)·NH·C₉H₉, one of which melts at 97–99°, the other at about 81–83°; similarly with *d*-hydrindamine, or with *l*-menthylamine, the chloride gives two isomeric amides. The more sparingly soluble compound is readily isolated in all three cases, but the more readily soluble one, which seems to form half of the original product, is not easily obtained free from its isomeride.

These results seem to prove that phenyl-*p*-tolylphosphoric acid is an externally compensated compound, and further experiments on the resolution of this and of similar derivatives of phosphoric acid are in progress.

PHYSICAL SOCIETY.

Ordinary Meeting, June 25th, 1909.

Dr. C. CHREE, F.R.S., President in the Chair.

A PAPER entitled "A Transition-point in Zinc Amalgam" was read by Prof. H. S. CARHART.

The paper gave the preliminary results of an investigation which has for its primary object the determination of the heat of dilution of zinc amalgams. This heat of dilution is negative; that is, the dilution of zinc amalgam by the addition of mercury absorbs heat. In the course of the experimental work, which was conducted by Dr. W. D. Henderson, phenomena so extraordinary were encountered that the speaker ventured to call the concentration at which they occur a transition-point in zinc amalgam.

The method employed was electrical, by means of a concentration cell, the only difference between the two legs of the cell of H-form being in the concentration of the amalgam composing the electrodes. The ratio of the zinc to the mercury, expressed as a percentage, was in every case twice as great in one leg of the cell as in the other. This relation was secured by weighing out pure mercury in two portions as one to two, and depositing in them the same quantity of zinc electrolytically by connecting the two in series with anodes of pure zinc, and both in series

with a silver coulometer. The operation was conducted in an atmosphere of hydrogen, and the concentration cell was exhausted of air and filled with hydrogen to avoid oxidation.

Such a concentration cell is reversible, and the Gibbs-Helmholtz equation applies to it. This equation is—

$$E = \frac{H}{nF} + T \frac{dE}{dT}$$

In this case the *H* stands for the heat of dilution only, all other forms of heat absorption or evolution being equal and of opposite sign on the two sides of the cell. The second term is the equivalent of the Nernst equation for the E.M.F. of a concentration cell, both being directly proportional to the absolute temperature *T*. It is then obvious that the Nernst equation applies only to solutions or amalgams so dilute that the heat of dilution is negligible. By measuring *E* at a known temperature and determining *dE/dT*, the equation gives the heat of dilution *H* in passing from any concentration to one half as great.

From a concentration of 0.5 per cent to about 2.2 per cent the electro-motive forces fall only slightly, and all lie on a straight line. The same is true of *dE/dT* and *H*. But at a concentration of about 2.3 per cent the line denoting E.M.F. abruptly changes direction downward, while the value of *dE/dT* increases five-fold. Also, the heat of dilution changes from negative 450 joules per grm.-mol. of zinc to negative 8700 joules. The three curves then again become nearly straight lines. When zinc amalgam of 3 per cent concentration is diluted to one-half, the absorption of heat is very nearly 10,000 joules per grm.-mol. of zinc. These abrupt changes indicate a transition-point in the zinc amalgam.

Mr. F. E. SMITH congratulated the author, and asked if it would be possible to obtain a zinc amalgam which could be used in a Clark cell so as to give a small temperature coefficient.

Prof. C. H. LEES expressed his interest in the experiments, and hoped that they would provide definite information as to the state of the zinc at the particular point described.

The AUTHOR, replying to Mr. Smith, said he had not given attention to the point raised, but it appeared to him that a Clark cell set up with zinc amalgam of a concentration below this transition-point would have a temperature-coefficient larger than that of the normal Clark cell.

A paper on "A Method of producing an Intense Cadmium Spectrum, with a Proposal for the Use of Mercury and Cadmium as Standards in Refractometry" was read by Dr. T. M. LOWRY.

Of the twenty-six wave-lengths that have been used in the study of rotatory dispersion (*Proc. Roy. Soc.*, lxxxi., p. 472, Nov. 19, 1908), the following seven have been found to be the most suitable for general use:—

Li	Cd	Na	Hg	Cd	Cd	Hg
6708	6438	5893	5461	5086	4800	4358

In refractometry it has been customary to use the series:—

H _α	Na	H _β	H _γ
6560	5893	4861	4341

This series has the disadvantages (1) that the chief standard, Na 5893, is a doublet, and (2) that the other three lines are of such weak intensity that they are useless for the majority of optical measurements. It is therefore urged that—in view of the readiness with which the mercury and cadmium spectra can now be produced—the mercury green line should be generally adopted in place of sodium as chief standard in optical work of all kinds, and that the hydrogen lines should be abandoned even as secondary standards in favour of the series of wave-lengths set out above. In support of this proposal it is pointed out that the green mercury line occupies a convenient position in the spectrum, is exceedingly brilliant and of such a high degree of purity that a sharp extinction can be obtained in reading a rotatory power of 5000°; that the cadmium lines are equally brilliant and of an even higher order of purity;

and that the wonderful intensity of the violet mercury line is more than sufficient to compensate for the drawback arising from the presence of two weak satellites. In the measurement of optical and magnetic rotatory dispersion, the ratio Hg 4358 to Hg 5461 is sufficient to characterise the substance under examination, and similar considerations will probably be found to apply in the measurement of refractive dispersion.

In order to produce a cadmium spectrum of sufficient intensity for polarimetric work, advantage is taken of the favourable properties of the silver-cadmium alloys. On account of their isomorphism the two metals form an excellent series of alloys which are characterised by good mechanical properties and very high melting-points (an alloy with 60 per cent Cd melts as high as $700^{\circ}\text{C}.$). In striking contrast to the behaviour of the pure metal, the alloy gives a steady arc which can be kept true to centre by rotating the electrodes in opposite directions. The spectrum shows the silver as well as the cadmium lines, but these are so far separated that even with a low resolving-power the slit of a spectroscope can be opened to its full width without any overlapping of the brilliant "blocks" of light which take the place of the usual "lines."

Mr. TWYMAN remarked that during the last few weeks he had seen a cadmium tube, similar to a mercury lamp, working with satisfactory results. Such tubes had been used for some time by Paschen and Röntgen. He agreed with the author with regard to the greater use of mercury light for spectroscopic and similar purposes.

Dr. A. E. H. TUTTON said that he had been working lately with cadmium tubes and found that they worked well for a considerable time. With regard to the measurement of refractive indices he was astonished that more use was not made in this country of the monochromatic illuminator, which he described some years ago. The instrument was used in Germany, and gave satisfactory results.

The AUTHOR said that in some cases it was necessary to work with many wave-lengths, and under such circumstances Dr. Tutton's monochromatic illuminator would be useful. It was also useful, however, to have seven wave-lengths as standard lights.

Mr. A. CAMPBELL read a paper "*On the Measurement of Wave-length for High Frequency Electrical Oscillations.*"

The experiments had for their object the calibration of wave-meters for the measurement of the high frequencies (200,000 up to 1,000,000 vibrations per sec.) used in wave-telegraphy. Two wave-meters (A and B) were tested, both being of the type consisting of a series of self-inductance coils used singly (L) in series with a variable air-condenser (K) and a thermo-ammeter, the reading of K being obtained by altering the capacity until the circuit shows resonance with the working circuit. The coils of wave-meter (A) were wound with solid wire, those of (B) with stranded wire ($7/36^s$), each strand being separately insulated. The absolute value of the frequency was determined by photographing spark-trains in the primary circuit by means of a rotating mirror running at a constant and accurately measured speed. As the following table shows, the value of the frequency n_1 deduced from the measured values of K and L with wave-meter (B) were in close agreement with the actual n deduced from the spark-photographs.

n .	n_1 .
Vibrations per sec.	Vibrations per sec.
290,300	290,500
516,800	516,800
818,000	821,200
1,042,000	1,039,000

With wave-meter (A) the agreement was naturally not nearly so close, but was much improved when the values of the self-inductances of the solid wire coils were corrected to the high frequency values by the formulæ of Heaviside and L. Cohen. The results in the above table show that the inductances of the stranded wire coils are practically unaltered for frequencies from 0 up to 1,000,000 vibrations per sec.

Mr. W. DUDDELL said the paper was a valuable one because accurate experiments on self-induction and capacity at high frequencies were required. With reference to the photographs he asked if the author had used his method to photograph arcs, and if so, with what results. It would be interesting to know how low it is possible to get the apparent resistance of a coil with high frequency currents by stranding the wire.

Dr. ERSKINE-MURRAY, referring to Mr. Duddell's remarks, said that in actual practice the resistance could not be reduced more than about 10 per cent by stranding.

Mr. TAYLOR congratulated the author, and pointed out that the wave-meters described could only be used at the transmitting station. Wave-meters were required which could be used at receiving stations. Referring to the question of stranding he pointed out that it was possible to overdo the stranding and obtain less satisfactory results than could be obtained by stranding with a fewer number of wires.

Mr. G. B. DYKE called attention to experiments similar to those described which were being carried out by Dr. Fleming at University College. With reference to the spark-photographs he was surprised that an accuracy of 1 in 1000 could be obtained.

The AUTHOR, in reply, stated that as the whole distributed capacity of the inductance coils had very little effect on the frequency of resonance, the dielectric hysteresis of the ebonite would be negligible except as regards damping. Sparks appeared to give sharper and more accurately measurable photographs than vacuum-tube discharges or arcs, except mercury arcs, which gave the clearest and best pictures.

A paper on "*An Electro-magnetic Method of Studying the Theory of and Solving Algebraical Equations of any Degree,*" by Dr. RUSSELL and Mr. ALTY, was read by the Authors.

They point out that the problem of finding the roots of an algebraical equation of the n th degree is identically the same as that of finding the positions of the "neutral points," that is, the points where the resultant force due to the earth and definite currents in n long vertical wires is zero. The n wires are arranged at any convenient distances apart in a plane which is at right angles to the magnetic meridian. The currents in the wires are then adjusted to certain values which are readily found by the methods of partial fractions. If x_1 and y_1 be the coordinates of one of these neutral points measured with reference to certain definite axes, $x_1 + y_1 \sqrt{-1}$ is a pair of roots of the original equation. All the real roots lie on the axis of X which cuts the wire at right angles. The positions of the neutral points thus determine all the roots real and imaginary of the given equation. The peculiar advantage of the method is that we can see, in many cases almost at once, what effect varying the value of the coefficient of any power of x will have on the roots of the equation. A simple apparatus which the authors have devised for students' use is described. The positions of the neutral points are determined by means of a small charm compass. In this way all the roots can be determined with a maximum inaccuracy of 1 per cent.

A paper entitled "*The Sine Condition in Relation to the Coma of Optical Systems*" was read by Mr. S. D. CHALMERS.

The condition for the correction of coma in a centred optical system is the well-known Sine condition. This has been proved by Clausius, Helmholtz, Hockin, and others, and the importance of this condition in the design of optical systems has been pointed out by Abbe, Steinheil, Conrady, and others. So far as the author is aware no discussion of the effects of failure to satisfy this condition has been published, and the present paper shows how to obtain the relation between the coma of a system and the errors in the sine condition.

Dr. C. V. DRYSDALE exhibited a new Fery Thermo-electric Calorimeter.

This form of calorimeter can be used continuously, and

permits the value of the gas produced in a gas-works or producer-plant to be watched from time to time. The principle of the instrument is that of burning the gas to be tested at a constant rate in a special burner consuming from 5 to 10 litres per hour. This burner heats a recuperative thermopile, of which the cold junction is traversed by the air employed for the combustion, while the hot junction is heated by the products of combustion. The thermopile contains 15 junctions which enables a P.D. of 0.2 volt to be obtained. The energy produced is sufficient to obtain a trace with a recording instrument similar to that obtained with the Richard recording thermometers and barometers.

Mr. R. S. WHIPPLE expressed his interest in the calorimeter and said he was surprised at the accuracy which could be obtained over large variations of the rates of consumption of the gas. There was a great need for a satisfactory calorimeter of the kind exhibited.

A paper by Mr. F. W. JORDAN on "An Instrument for Measuring the Strength of an Intense Horizontal Magnetic Field" was read by the author.

The method consists in measuring directly the transverse force on a conductor traversed by a current in a direction at right angles to the field. Two copper strips of uniform width, each cut to form three sides of a rectangle, are fastened together and connected by short tinsel leads to terminals, so that the current can be sent in the same direction through each of the insulated conductors. The framework is suspended in the field to be measured from a helical spring of phosphor-bronze. The tension in the spring can be adjusted to bring the framework into a sighted position. To make a measurement the horizontal conductors are arranged at right angles to the field, and a known copper weight is suspended from the centre. A current is passed through the wires and its strength adjusted until the framework is again in its sighted position. The strength of the field is then easily calculated. The results obtained with the apparatus using fields from 1000 to 13000 gaussses agreed with those got by the ballistic method to 1 part in 400.

Papers by Prof. POYNTING and Mr. TODD "On a Method of Determining the Sensibility of a Balance," and by Mr. TODD on "The Balance as a Sensitive Barometer" were taken as read.

NOTICES OF BOOKS.

Chemical Technology and Analysis of Oils, Fats, and Waxes. By Dr. J. LEWKOWITSCH, M.A., F.I.C. Fourth Edition. London: Macmillan and Co., Ltd. 1909.

THE fourth edition of this well known standard treatise on oils, fats, and waxes represents practically a new book, as the scope has been so greatly widened to meet the demand for a work covering the whole subject. Hence it has been found necessary to divide the work into three volumes instead of two. In the first the arrangement is practically unaltered, the classification, constitution, and chemical methods of examining oils, fats, and waxes being treated in detail with the results of modern investigations. Volume II. consists of a series of monographs dealing with technology, while the third volume discusses manufacturing processes, those which have recently been worked out being fully treated.

Tables of Properties. By WILHELM SEGERBLOM, A.B. Exeter, N.H.: Exeter Book Publishing Company. 1909.

THIS book, which is to be used as a reference book in the laboratory for corroboration of the results given by tests in ordinary qualitative analysis, contains tabular statements of the properties of some 1500 common inorganic substances. The metals are arranged in six groups, following the classi-

fication of Fresenius, and thirty-six salts of each metal are included. A special section is devoted to acids, and another comprises all the non-metals and rare elements together. Only constant use can satisfactorily test the perfect accuracy of the data contained in the book, but there can be no question about the convenience of its arrangement for rapidity of reference. The common as well as the chemical names of all the salts are given, and the indexing is thorough. One criticism may be made, namely, that although some physical constants such as melting-points and boiling-points are given, additional data relating to solubility would have been useful.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlviii., No. 22, June 1, 1909.

Oxides of Uranium.—Echsner de Coninck.—The author proposed to transform uranic sulphate into nitrate by treating a dilute aqueous solution of it with neutral barium nitrate until all the barium sulphate had been precipitated. The liquid was then concentrated and evaporated to dryness, when the light yellow uranic hydrate, $\text{UO}_3 \cdot 2\text{H}_2\text{O}$, was deposited, mixed with a very minute amount of orange-yellow monohydrate, $\text{UO}_3 \cdot \text{H}_2\text{O}$. From a mixture of uranous and uranic sulphates, uranic dihydrate and uranous monohydrate $\text{UO}_2 \cdot \text{H}_2\text{O}$ were obtained. The latter oxidises spontaneously in air, as shown by the equation $\text{UO}_2 \cdot \text{H}_2\text{O} + \text{O} = \text{UO}_3 \cdot \text{H}_2\text{O}$.

Subchloride of Chromyl.—P. Pascal.—Nitric oxide acts on chromyl chloride to give a subchloride of chromyl, $5\text{CrO}_2\text{Cl}_2 + 4\text{NO} = (\text{CrO}_2)_5\text{Cl}_6 + 4\text{NOCl}$. This compound forms crystals which have magnetic properties. They deliquesce in damp air, and dissolve readily in water, giving chromic acid, hydrochloric acid, and salts of chromium. At a high temperature they decompose according to the equation $3(\text{CrO}_2)_5\text{Cl}_6 = 5(\text{CrO}_2)_3\text{Cl}_2 + 8\text{Cl}$, while, when gently heated, the reaction which occurs is $(\text{CrO}_2)_5\text{Cl}_6 = (\text{CrO}_2)_3\text{Cl}_2 + 2\text{CrO}_2\text{Cl}_2$. It may be said that at a relatively low temperature the subchloride's reactions are due to its chlorine, and at a high temperature to both its oxygen and chlorine. In many of its reactions it behaves like chromyl chloride, CrO_2Cl_2 , except that, in general, heat has to be applied to induce its reactions.

MISCELLANEOUS.

The Oat Crop.—The Board of Agriculture and Fisheries have received information as to damage done to the oat crop during the present year by the Stem Eelworm and the Frit Fly. The Board desire to inform farmers that copies of leaflets on the subjects may be obtained gratis and post free from the Secretary, Board of Agriculture and Fisheries, 4, Whitehall Place, London, S.W. Letters so addressed need not be stamped.

Presentation of the Albert Medal to Sir Andrew Noble.—The Council of the Royal Society of Arts attended at Marlborough House on the morning of the 8th inst., when his Royal Highness the Prince of Wales, President of the Society, presented its Albert Medal to Sir Andrew Noble, Bart., K.C.B., D.Sc., D.C.L., F.R.S., "in recognition of his long-continued and valuable researches into the nature and action of explosives, which have resulted in the great development and improvement of modern ordnance."

THE CHEMICAL NEWS.

VOL C., No. 2591.

RELATIONS BETWEEN THE INACTIVE GASES AND THE RADIO-ACTIVE ELEMENTS.

By F. H. LORING.

THE phenomenon as revealed by radio-active substances, whereby atomic disintegrations and molecular dissociations are brought about, has suggested that the Mendeleeff periodic classification, though not an exact generalisation, if such a term may be used, is an index of an underlying process of evolution. Such a process implies the building up of the elements from some primordial stuff. This doctrine has led to a great deal of useless speculation. We are, however, face to face with a few extraordinary elements that undergo change and act as powerful disintegrators when applied to other substances.

Quoting from Soddy's popular book, "The Interpretation of Radium," p. 142:—"The question, how can an element or the atom of an element change, has given rise to many arguments of etymological rather than scientific importance. What we now certainly know, and what radio-activity has given us for the first time the opportunity of learning, is, first, that some elements *do* change, and secondly, *how* they change. The element radium changes by the loss of an atom of helium* into the emanation, which is about as different from radium in its chemical or material nature as two elements well could be. The one is a member of the group of alkaline earths, the other of the argon family of elements. After all, is not this rather to be anticipated? When we arrange the elements in the order of their atomic weights—an arrangement which led to the recognition of what is known as the Periodic Law—the most sudden and surprising differences appear between succeeding elements. Chlorine, potassium, and argon are the three succeeding elements in such an arrangement, and there is no resemblance whatever between them. In the nine successive transformations radium undergoes, the atom suffers, in most but not in all, a disintegration in which a helium atom is expelled. The heavy residues of the original atom, remaining after the successive loss of one, two, three, and so on of these helium atoms, constitute the intermediate bodies—the emanation, radium A, radium B, and radium C—successively produced each from the preceding. It is therefore rather to be expected that the succeeding transition substances produced one after the other should differ entirely from one another in their material characteristics, and this, so far as we have been able to discover, is fully borne out."

It may not be out of place to refer here to Sir William Crookes's "figure-eight" model, illustrating the periodic law, and involving in its conception three dimensions, which is highly suggestive, since Nature, as he has said, works in three fundamental directions. This may also represent an approximation to a truth which would repay further investigation. Instead of a single line so looped as to take all the elements, several such lines in parallel may more accurately co-ordinate the weights. It may be objected that such a system is not simple enough, but, on the other hand, those who look for extreme simplicity are likely to be disappointed, as the vast complexity of Nature renders simple relations of this kind extremely improbable. Whatever the intrinsic complexity of the system may be probably matters little, so long as accurate results are obtained and the method is comprehensive and regular.

* The work of Gray and Ramsay (*loc. cit.*) throws considerable doubt upon the theory that single atoms of helium differentiate by weight the successive elements, since the emanation has probably a weight not far from 176.—F.H.L.

The system I devised (see CHEMICAL NEWS, xcix., 148 and 241) fulfils the condition of accuracy and regularity to an extent that enables the weights of the elements to be corrected to the second decimal place in most instances, but here again the proof of its validity is subject to criticism, since there is no absolute reason to believe that all the elements would fit into the system proposed. There are two notable exceptions in nitrogen and beryllium. On the other hand, the validity of the system seems to be strengthened, since the prediction by its means of an inert or inactive gas having an atomic weight of 174.98 is practically fulfilled. This element answers to the radium emanation mentioned above, the figure agreeing fairly well with the value worked out recently by Gray and Ramsay (*Journ. Chem. Soc.*, June, 1909, p. 1073). They have, by plotting the weights of the higher inactive gases against their boiling-points (*a*), critical temperatures (*b*), and pressures (*c*) respectively, obtained three regular curves (arcs of a circle), each of which gives 176 (*a*, *b*, and *c* being determined for the emanation), or a value slightly below this figure (apparently lower in the case of the critical pressure curve) as the atomic weight of the emanation.

(NOTE.—An early attempt to determine the molecular weight of the radium emanation by diffusion was made by Rutherford and Miss Brooks (*Trans. Roy. Soc. Canada*, 1901-2, 2nd Series, Sec. III., p. 21), but the values obtained gave a molecular weight between 40 and 100. P. Curie and Danne (*Comptes Rendus*, 1903, cxxxvi., 1314), who measured the inter-diffusion constant for the emanation by passing it through capillary tubes into air, obtained a value of the same order; while Bumstead and Wheeler (*Am. Journ. Sci.*, 1904, xvii., 97), employing a porous plate, arrived at 180 as the weight of the emanation. Makower (*Phil. Mag.*, 1905, ix., 56) arrived at a figure ranging from 85 to 97, using in his experiments porous plugs of different materials. Perkins (*Am. Journ. Sci.*, 1908, xxv., 461), comparing the diffusion of the emanation with that of mercury vapour, using also a porous body, obtained by the usual application of Graham's law, 235—a weight higher than that of radium itself. It is thought that the high value was due to experimental errors. Referring to the emanations of actinium and thorium, Bruhat (*Comptes Rendus*, 1909, cxlviii., 628) determined the diffusion of actinium emanation and calculated therefrom the molecular weight. Russ (*Phys. Soc.*, paper read November 27, 1908; *Phil. Mag.*, 1909, xvii., 412) determined the relative diffusion of the actinium and thorium emanations (ratio 1.19), which gives the molecular weight ratio (1.19²) as 1.42, and since the determinations of diffusion by Bruhat and Russ are in themselves concordant, the molecular weight of the actinium emanation comes out at about 70 and that of thorium at 100. It will be seen from the above that the diffusion experiments cited yield widely divergent results (although the Bruhat and Russ measurements are apparently sound, judging from the check determinations made), and the values so obtained in several instances indicate molecular weights that either do not agree amongst themselves or the values are not what one should expect from a study of the periodic table if the gases are monatomic and inactive as is supposed. It is therefore reasonable to conclude that further evidence is necessary to establish the weights as determined indirectly by diffusion methods).

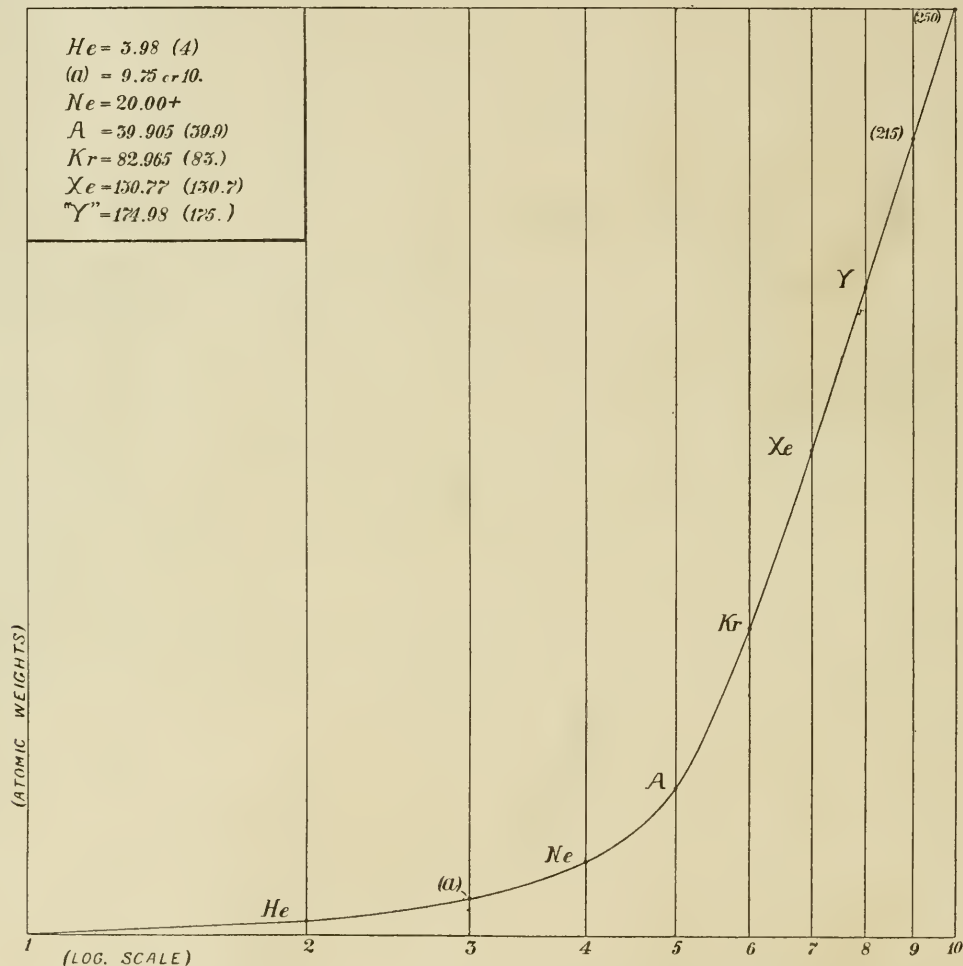
It is, perhaps, worth noting that in my system *four* inactive gases (He, Ne, Ar, and Kr) were intersected by the "first" circle, and only *three* (unless mercury is included) by the second one of the same radius, but a further proof of a tabular regularity or symmetry, based on the elliptical intersections, was shown.

Gray and Ramsay, moreover, show that by adding fairly uniform differences (*e.g.*, 44) to preceding elements of the same series, the succeeding values 175, 219, and 263 are obtained. A Mendeleeff table is shown with similar differences between adjacent groups to support these extensions. The two latter values may be too high, since, by

another method that incidentally throws some light on the nitrogen difficulty referred to above, lower values may be obtained.

A. Ham (*Assoc. Ing. El. Liège Bull.* 5, June, July, and August, 1905, 354) draws attention to the advantages which in a number of cases result from the use of logarithmically ruled paper. As a first example, he considers the case in which the relation connecting two quantities y and x is suspected to be of the form $y = ax^m$. Since in this case $\log y = \log a + m \log x$, it follows that if the law holds good, then on plotting $\log x$ as abscissa and

some probable degree of accuracy. Such a curve is here shown, which is a half-scale reduction from standard paper (250 mm. $\times$ 250 mm.), the weights being measured off in mm. on the vertical lines 2, 3, 4, &c. The blue horizontal rulings of the original are not reproduced. The figures in parentheses may be regarded as "rounded off" values, the others being those which were corrected or determined by the system of ellipses and circles, based on the formula $3 \cdot 1 \pm 4^n$, ± 2 difference from 0 to 0.9 = the atomic weight; the differences being plotted as atomic weights against the position of the elements established by the



$\log y$ as ordinate, the relation will be represented by a straight line, and the values of a and m are immediately obtainable. A similar method may be used with functions of the form $y = ae^{mx}$ (quoted from *Sci. Abs.*, 1906, A, 236).^{*} This method of analysis does not, of course, give a straight line when the weights of the inert gases are plotted on doubly-ruled logarithmic paper, but if paper is selected which is ruled only one way (technically known as "half-" or "semi"-log paper) the weights plotted as vertical ordinates give a curve that is not reflex. The latter portion of the curve approximates to a straight line, and enables the extreme values to be extrapolated with

equation, with the result that they fall on regularly grouped ellipses with common foci.

It was found necessary to assume a blank (a) in order to get a probable curve with a zero origin, and the value of a appears to be 9.75 or 10, which, it is significant to note, added to that of helium, 3.98 or 4.0, gives the value for nitrogen. 9.75 falls on the first circle (see *CHEMICAL NEWS*, xcix., 148, referred to above), which value, together with the hypothetical satellite (0.27) previously deduced and helium (3.98), gives practically the exact figure for nitrogen.

It will be seen that the two highest values are slightly below those indicated by the periodic table, but having regard to the tendency of the elements of high atomic weight to undergo spontaneous disintegration, or not to exist owing to the instability of the atom, the lower values seem more probable. The curve is perhaps drawn too

^{*} See also Mellor's "Higher Mathematics for Students of Chemistry and Physics," 3rd ed., p. 331. Functions obeying the compound interest law will plot on semi-log paper as a straight line, as in the case of either $x + \log y = \text{constant}$, or $y + \log x = \text{constant}$.

straight at the finish, and slightly higher values, 216 and 251, might be assumed, which are still below those cited by Gray and Ramsay. It seems more probable that an element having an atomic weight above 260 would be radio-active and undergo spontaneous disintegration. Such an element might answer to actinium. Therefore, if actinium is 267, and its emanation 251, uranium 239, and uranium X 235, the following series, in which the second differences are in inverse geometrical progression, may be constructed :—

	235 = Ur X	
8 — 4 —	239 = Ur	} The elliptical curves are not established for such high and uncertain values.
4 — 12 —	251 = Ac Em	
4 — 16 —	267 = Ac	

In like manner, if 216 is the thorium emanation, another similar series is suggested thus :—

	200 = Hg	
8 — 4 —	204 = Tl	} If mercury is taken at 200, and is plotted above hydrogen, it falls on the second circle.
4 — 12 —	216 = Th Em	
4 — 16 —	232 = Th	

These series lead to the construction of one terminated by radium, and assuming its value to be 224·97 (practically 225) instead of 226, this similar series becomes :—

	82·97 = Kr	
4 — 44 —	126·97 = I	} Except in the case of radium, which falls below hydrogen, these values are in vertical alignment. They all practically fall on the elliptical curves.
2 — 48 —	174·97 = "Y" = Ra Em	
50 —	224·97 = Ra	

Finally, a fourth series based upon the theoretical values of argon, iron, bromine, and silver, as indicated by the curves, may be represented thus :—

	(39·90)	
16 — 0 —	39·90 = A	} These values fall on the curves in vertical alignment above hydrogen.
8 — 16 —	55·90 = Fe	
4 — 24 —	79·90 = Br	
28 —	107·90 = Ag	

Objection may be taken to the somewhat hypothetical series above shown owing to the absence of sufficient experimental evidence, and the values in some cases may not be considered as even probable. But I believe that the treatment is new, and that it may be worth putting to the test when more accurate data is available. Because a method does not agree with all facts, it does not follow that it is altogether bad.

Silver is not appreciably radio-active, consequently the last group does not harmonise very well with the previous ones, but the extreme sensitiveness to light of some of the silver compounds helps to complete the analogy. It will be seen that the most stable elements head each quaternian series until exceedingly high values are reached, and, just as uranium evolves uranium X, so radium evolves radium emanation. The curious position of mercury seems to suggest that a line of similar elements may be evolved from the radio-active disintegrations, bearing in mind that the ultimate product of radium appears to be a substance resembling lead.

7, Doughty Street, London, W.C.,
July, 1909.

AN APPROXIMATE DETERMINATION OF THE BOILING-POINTS OF METALS.*

By H. C. GREENWOOD, M.Sc.,
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DESPITE the facility with which high temperatures can be reached and maintained constant by means of electric heating, no general investigation of the boiling-points of the metals has yet been carried out, and such information as is available has in many cases been obtained by considerable extrapolation. Moreover, the published data are remarkably discordant, as will be seen from the individual results quoted below.

In the course of an extended experimental investigation, H. Moissan (*Comptes Rendus*, 1906, cxlii., 425) has made observations on the vaporisation of metals at high temperatures by observing the loss of weight of a considerable mass of metal heated for definite periods of time in his arc furnace. O. P. Watts has attempted to deduce from these experiments approximate values for the boiling-points of the metals (*Trans. Amer. Electrochem. Soc.*, 1907, xii., 141). In addition to the uncertainty due to the fact that many metals possess a high vapour tension at temperatures much below their actual boiling-points, considerable errors are caused by the fact that Moissan does not appear to have measured the expenditure of energy in the furnace, which varies widely according to the conductivity of the vapours surrounding the arc. Also, in many of his experiments the temperature of ebullition must have been altogether modified by carburisation.

Since it is now possible to perform effectively the heating and to make relatively accurate temperature measurements in the region concerned, the remaining difficulty is largely due to our ignorance of any material capable of remaining gas-tight at sufficiently high temperatures.

For approximate measurements it has, however, been found possible to circumvent this difficulty and yet obtain a sufficiently definite proof that actual boiling is taking place.

In the present investigation the following metals have been studied :—Aluminium, antimony, bismuth, chromium, copper, iron, lead, magnesium, manganese, silver, tin.

Experimental Methods.

In some unpublished work carried out by Dr. L. Bradshaw in this laboratory, measurements were made of the loss in weight of a crucible, containing the metal under investigation, maintained for a definite time at constant temperature; it being hoped that, by repeating the measurements at fixed points over a wide range of temperature, the loss by volatilisation would enable a fairly close approximation of the boiling-point to be deduced. It was found, however, that the volatilisation occurs over such a large temperature interval that in starting the present investigation other methods were resorted to.

In the first place thin-walled crucibles, containing a considerable amount of metal, were heated, either in a Moissan arc furnace† or in a carbon tube furnace, the energy consumption being kept constant and chosen so as to be capable of ensuring in the enclosure a temperature considerably higher than the boiling-point of the metal under investigation.

During the heating the temperature of the outside wall of the crucible was measured at regular intervals by means of an optical pyrometer; it being anticipated that when the relatively large mass of metal entered into ebullition some definite indication would be obtained that the crucible walls ceased to show an increase in temperature. The measurements, however, were distinctly disappointing, the crucible walls rising considerably above the boiling-point of the metal.

* A Paper read before the Royal Society, May 27, 1909.

† This method was employed by Féry (*Ann. Ch. m. Phys.*, Ser. 7, vol. xxviii., p. 425). His values are 1040° C. for zinc and 2100° C. for copper.

The method eventually adopted was to employ a vertical carbon tube resistance furnace (*cf.* Hutton and Patterson, *Trans. Faraday Soc.*, i., No. 2, p. 187), in which was suspended a long graphite crucible which contained the metal under investigation (see Fig. 1). The depth of metal employed was usually about 30 mm.* Temperature readings of the outer walls of the crucible were taken by means of a Wanner optical pyrometer, a side tube being provided exactly opposite the lower end of the crucible, and being so arranged that only the radiation from the crucible walls could fall on the pyrometer; the side tube was kept clear of vapours by a current of hydrogen.

The temperature of the heating tube, which could be readily raised to 2700°, was under delicate control by adjustment of the current passing through it.

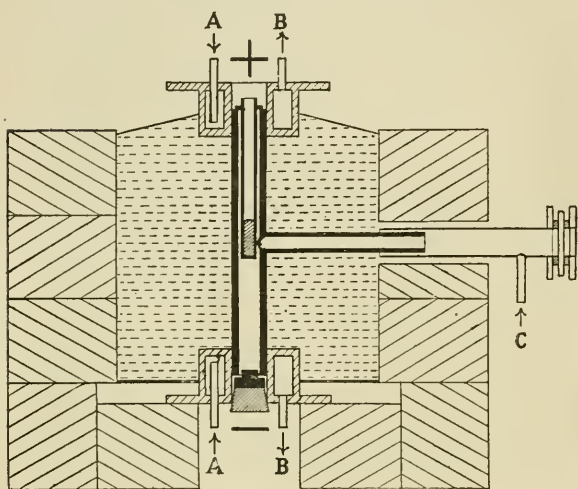


FIG. 1 (Scale 1 : 8).

Resistance furnace, consisting of vertical carbon tube electro-coppered at the ends and soldered into brass castings provided with water circulation at A and B. Temperature readings taken down the side tube of carbon, fixed into a brass tube with a window at the end, a current of hydrogen being admitted at C. The whole furnace was packed in crushed wood charcoal, while a thin-walled graphite crucible contained the metal to be studied,

The measurements of the boiling-points were carried out by slowly raising the temperature of the crucible and observing the surface of the metal from above through an absorbing glass. At first the surface of the molten metal remains perfectly still, but as the boiling-point is approached a slight agitation of the surface is observed which soon becomes vigorous. In the case of most of the metals studied, the difference between the temperature indicated when a gentle agitation is first apparent, and that at which the ebullition has become so violent that globules of metal are being ejected from the top of the tall crucible, does not exceed 100°. By taking the boiling-point as that temperature at which ebullition becomes decided, quite concordant results were obtained in different experiments, as will be seen from the detailed measurements in three experiments with silver, given in the accompanying tables.

From the study of a large number of metals in this manner, it appears probable that the temperature at which the vaporisation becomes sufficiently rapid to cause a decided projection of drops from the surface may be taken with fair approximation as the boiling-point; in the three experiments quoted this temperature is 1955°.

The question as to whether the temperatures measured on the outer surface of the crucible really indicate suffi-

* The tall crucible employed acts as a reflux condenser, so that the quantity of metal does not rapidly decrease. Moreover, comparative experiments proved that wide variations in the height of the metal had no influence on the boiling-point indicated.

Time from commence- ment. Mins.	Tem- perature. °	Current amperes.	
I.			
12	1800	320	Clear and still.
13	1820	320	
14	1860	320	
15	1905	330	Clear, gentle agitation at edges, centre still.
16	1915	330	
17	1935	330	All surface in gentle agitation no drops thrown up.
18	1935	330	
19	1955	330	Drops thrown up very gently.
20	1955	330	
21	1965	330	Drops quite decided.
22	1975	330	
			Drops thrown half way up crucible.
21	1965	330	Drops sent out of crucible.
22	1975	330	
II.			
16	1770	260	Perfectly clear and still.
18	1815	260	
20	1860	260	
21	1875	290	Slight trace of movement at edges.
22	1880	290	
23	1915	290	Surface quiet.
24	1925	290	
25	1955	290	Gentle agitation, no drops thrown up.
26	1955	300	
27	1975	300	Decided agitation, drops thrown up gently.
28	1975	300	
29	1980	300	Drops half way up crucible.
			Vigorous, drops projected out of crucible.
III.			
6	1440	330	Clear and still.
9	1560	330	
12	1670	360	
13	1730	360	
16	1790	360	
18	1840	370	
20	1860	370	
21	1880	380	Slight agitation at edges.
22	1900	380	
24	1920	380	Clear, gentle agitation all over surface.
25	1935	390	
27	1955	390	Agitation decided, no drops thrown up.
29	1980	390	
30	2000	390	Agitation decided, occasional drops.
			Drops sent up decidedly.
			Drops vigorous, half way up crucible.
			Drops projected out of crucible.

ciently accurately the actual temperatures of the metal is certainly an important one. Measurements made up to 1500° in comparison with a thermo-element indicate that the difference is not very great, but in order to obtain further confirmation and attempt to make use of a somewhat different method of measurement, an apparatus as shown in Fig. 2 was employed. Here the heating is effected from the inside by a rod of carbon, an annular crucible containing the metal, and the temperature being read on the outer surface of the crucible as before; thus reversing the effect of errors in temperature measurement due to the thermal conductivity of the crucible walls, and altogether removing any possibility of reflection of the radiation from the hotter surface of the heating tube.

Experiments made with lead proved a close agreement between the results obtained by the two methods, but all attempts to obtain limitation of the temperature of the outer wall whilst the metal was boiling, and when the heating rod was maintained at an excessively high temperature, proved abortive.

The current of hydrogen which was passed through the side tube of the furnace (shown in Fig. 1) was found to have quite a marked influence on the ebullition of the

metal. If the current of hydrogen is stopped when the metal is gently boiling ebullition ceases. Moreover, when nitrogen was employed instead of hydrogen, the temperature readings were concordant in similar experiments, but were always considerably higher (50° to 1000°) than those obtained in a hydrogen atmosphere.

This curious and unexpected effect appears to be due to the ease with which hydrogen permeates the crucible walls, removing and diluting the column of heavy vapour. If, after interrupting the admission of hydrogen for a brief period, the stream be re-started, it can be distinctly seen, on looking down the crucible, that the vapours above the metal surface are immediately dislodged by gas passing through the crucible walls. Using a slow current of nitrogen, on account of its much higher density, the values obtained are practically the same as if no gas at all were admitted.

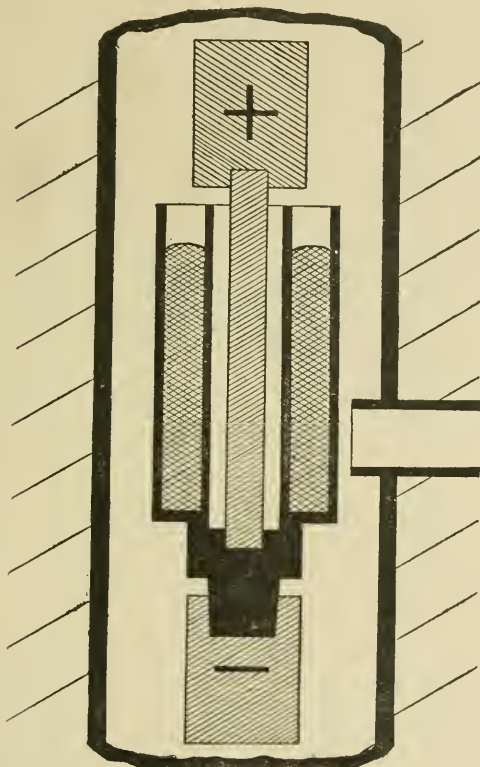


Fig. 2 (Scale 2 : 5).

Annular crucible turned out of graphite, heating being effected electrically by means of the central carbon rod, which is supplied with current from the two thick graphite rods. The crucible is fixed inside a long wide carbon tube surrounded by kieselguhr, and temperature readings taken through a side tube just as with the apparatus shown in Fig. 1.

A large number of measurements were made in a nitrogen atmosphere and the results are indicated below, but it seems probable that the values obtained with hydrogen approximate more closely to the boiling-points of the metals at atmospheric pressure.

The use of a graphite crucible is naturally limited to such metals as do not appreciably combine with, or dissolve, carbon under the conditions of the experiment. As will be seen, modifications have to be introduced in the case of other metals.

Temperature Measurements.

Throughout this investigation the temperatures have been measured by a Wanner pyrometer sighted on the outer wall of the crucible containing the metal. This was

made possible by the provision of a side tube as shown in Fig. 1, the tube being kept free from vapours by a current of hydrogen.

In order to ensure the accuracy of the temperature readings, the current passing through the standard lamp of the pyrometer was carefully adjusted, an ammeter being included in the lamp circuit. Comparison with a thermo-element up to 1500° C. (using the correction for the difference between the optical and thermo-electric scales of temperature) (*cf.*, Burgess, *Trans. Am. Electrochem. Soc.*, xi., 247) showed that the temperature scale provided with the instrument closely concurred with the measurements of the thermo-element.

In order, however, to render the results capable of subsequent correction, the pyrometer was standardised by measuring the "black body" temperatures of the melting-points of platinum, rhodium, and iridium. These metals, which were specially prepared of a high degree of purity by Messrs. Johnson, Matthey, and Co., were used in the form of strips 4 mm. wide by 8 cm. long, and were heated electrically, the pyrometer being sighted upon them.

The individual values, as measured with this pyrometer under identical conditions to the measurements for the boiling-points, were as follows:—

	Platinum.	Rhodium.	Iridium.
	1545	1670°	1995°
	1560	1655	1985
	1555	1680	2025
	1545	1680	1990
	—	1680	2035
	—	—	—
Mean.	1551	1673	2006

Holborn and Henning (*Sitzungsber. K. Akad. Wiss.*, Berlin, 1905, xii., 311) give the following "black body" values of the melting-points:—Platinum, 1545° ; rhodium, 1650° ; iridium, 2000° .

In view of the fact that such fixed points can readily be determined and consequently the relative accuracy of the measurements given in the present work may be conveniently checked, it has been thought best to publish the results as they were obtained, without correction, it being clearly understood that the temperatures are all given on the optical scale.

The only correction introduced is a deduction of 20° from the values in the summary for temperatures below 1500° , as these were determined without any absorption glass before the pyrometer and standardisation under these conditions indicated this difference of 20° .

The main object of the investigation was to obtain approximate values for the boiling-points measured under closely similar conditions, and thus clear away the uncertainty of the published data, which in several cases amounts to some hundreds of degrees. In order to obtain more accurate results, it remains to introduce refinements in the method which it was impossible to adopt in an attempt to extend the work over a large number of metals.

Copper.—Practically the only determination previously recorded of the boiling-point of copper is that of Féry (*Annales de Chimie et de Physique*, 1903, sér. 7, xxviii., 428), his value being 2100° C. Wartenberg (*Zeit. Anorg. Chemie*, 1908, lvi., 320), from measurements of the vapour densities of the metals, and by observing at what temperatures they begin to assume the gaseous state rapidly, deduced approximate values for the boiling-points of a few metals; he classes copper with tin and aluminium as probably above 2200° C.

When measurements were made by the general method described above the different stages of the vaporisation were sharply indicated, a very clear surface of the metal being visible throughout.

The following results were obtained for electrolytic copper at intervals of several months, the atmosphere being hydrogen, which was admitted through the sighting tube for the pyrometer.

First gentle agitation of surface.	Decided ebullition.	Violent ejection of material from the crucible.
2250°	2300°	2350°
2300	2320	
2280	2320	2400
2230	2275	
2275	2320	2375

Boiling-point. Mean approx. 2310°.

In nitrogen, as explained previously, the readings are considerably higher; the first agitation of the surface occurring at 2430°, decided ebullition at 2450°, and violent projection of material at 2475°.

An examination of the copper subsequent to the experiments indicated that a small amount of carbon had been dissolved, and, upon cooling, given up in the form of graphite.

Tin.—Carnelly and Williams (*Journ. Chem. Soc.*, 1879, p. 563) attempted to measure the boiling-points of some metals by suspending above the surface of the highly heated metal small iron or fire-clay tubes containing metals of known melting-point; they record the boiling-point of tin as between 1435° and 1505° C. (melting-point of nickel and iron), and state that it boils very well, and is more easily volatile than lead.

Wartenberg (*loc. cit.*), on the other hand, gives a probable value above 2200° C.

Moissan's experiments indicated that tin is less volatile than copper.

In the direct measurements made by the method described, the surface of the molten lead remained very clearly visible, and the different stages were sharply indicated. The following values for tin were obtained in a hydrogen atmosphere:—

First gentle agitation of the surface.	Decided ebullition.	Violent ejection of material from the crucible.
2150°	2275°	2320°
2100	2250	2300
2150	2250	2300
2210	2295	2350
2200	2270	2340
2150	2270	2320
2170	2250	2300

Boiling-point. Mean approx. 2270°.

In nitrogen the first general agitation of the surface occurs at 2220°, ebullition at 2350°, and violent projection of material at 2400°.

On subsequent examination, the metal did not appear to have been appreciably affected by the carbon.

Silver.—The value deduced by Wartenberg (*loc. cit.*) from his vapour density determinations is 2070° C. With silver assaying 99.9 per cent the following results were obtained in hydrogen, the readings being very concordant:—

First gentle agitation of the surface.	Decided ebullition.	Violent ejection of material from the crucible.
1900°	1955°	1975°
1915	1955	1975
1915	1960	2000
1900	1955	2000

Boiling-point. Mean approx. 1955°.

Silver is apparently very little affected by the carbon with which it was in contact at these high temperatures.

In nitrogen the first gentle agitation occurs at 2020°, ebullition at 2050°, and projection of material at 2075°.

Lead.—Carnelly and Williams (*loc. cit.*) give the boiling-point as between 1435° and 1505° C., whilst Wartenberg estimated it at 1580° C.

With Merck's "extra pure" lead, the following direct determinations were made in a hydrogen atmosphere:—

First gentle agitation of the surface.	Decided ebullition.	Violent ejection of material from the crucible
1475°	1520°	1585°
1475	1505	1540
1470	1540	1580
1475	1525	1600
1475	1525	1570

Boiling-point. Mean approx. 1525°.

In nitrogen the first gentle agitation of the surface commences at 1525°, boiling is distinctly visible at 1570°, and projection of material at 1600°.

Bismuth.—Carnelly and Williams found the boiling-point to be between 1084° and 1435° C. (melting-point of copper and nickel); Barus, by extrapolation from the values obtained at low pressure, gives as the approximate boiling-point at atmospheric pressure 1550° C. (*Bull. U.S. Geolog. Survey*, No. 103; *Am. Journ. Sci.*, [3], xlviii., 332).

Using Merck's "extra pure" bismuth, the following readings were obtained in hydrogen, the surface of the metal being somewhat obscured above 1425° C. by the condensing metallic vapours. After the experiment the metal seems to be quite unchanged.

First gentle agitation of the surface.	Decided ebullition.	Violent ejection of material from the crucible.
1415°	1435°	1460°
1400	1425	1480
1420	1450	1500
—	1450	1500

Boiling-point. Mean approx. 1440°.

In nitrogen the values deduced are 1450° for agitation of the surface, 1500° for boiling-point, and 1530° for violent boiling.

Antimony.—Several measurements have been recorded. Carnelly and Williams state that it lies between 1084° and 1435° C., Mensching and Meyer above 1437° C. (*Annalen*, 1887, ccxli., 317), and Biltz and Meyer 1500° to 1700° (*Ber.*, 1889, xxii., No. 1, 725).

Although the observation of the surface of the metal is in this case rendered somewhat difficult by the clouds of metallic vapour, the readings were fairly consistent.

The metal employed was Merck's "extra pure" antimony, and was apparently little affected by carbon after prolonged boiling.

First gentle agitation of the surface.	Decided ebullition.	Violent ejection of material from the crucible.
1420°	1455°	1500°
1400	1450	1470
1425	1470	1510
1425	1460	1505

Boiling-point. Mean approx. 1460°.

In nitrogen the corresponding values were 1480°, 1530°, and 1570°.

(To be continued)

Institute of Chemistry—Pass List, June-July Examinations, 1909. Of twenty-nine candidates who presented themselves for the Intermediate Examination, the following seventeen passed: W. Caw; A. P. Clark; R. L. Collett, B.A. (Cantab.); W. Dickson; S. Elliott; R. H. Ellis; N. Evers; J. E. Hackford; A. D. Heywood; F. E. Laughton; J. R. Nicholls; W. M. Paulley, B.A. (Cantab.); G. C. Petrie; E. F. Pollock; S. Robertson; T. Schwarz; and J. A. L. Sutcliffe. One candidate presented himself for a General Examination for the Associateship, and passed: L. Knight, A.R.S.M. Six candidates presented themselves for the Final Associateship Examination in the Branch of Mineral Chemistry, and four passed: H. L. Allen, B.Sc. (St. Andrews); R. H. Findlater; R. Gawler, B.Sc. (Leeds); and G. A. Smiley, B.Sc. (Lond.). In the Branch of Metallurgical Chemistry, of five examined three passed: A. Marcan; A. Marks, A.R.C.Sc. (Lond.); and A. W. Schultz, A.C.G.I. Of seven candidates who presented themselves in the Branch of Organic Chemistry, the following three passed: R. Boyd, B.Sc. (Glas.); C. S. Garland, B.Sc. (Lond.); A.R.C.Sc. (Lond.); and J. Young. In the Examination in the Chemistry of Food and Drugs, and of Water, of nine who presented themselves five passed: F. S. Aumonier; W. G. Carey; R. D. Carty, A.R.C.Sc.I.; T. R. Greenough, B.A. (Cantab.); and C. E. Sage. One of the candidates, C. E. Sage, was examined for the Fellowship.

A GRAPHITE CATHODE DISH.*

By J. W. TURRENTINE.

IN conducting a laboratory course in applied electrochemistry, one devoted largely to that phase of electrochemistry which has to do with solutions and the electrolysis of solutions, the need has been experienced for some good material which could be substituted for platinum in the construction of insoluble electrodes. Platinum, to be sure, makes the ideal insoluble electrode, but its cost makes the matter of supplying a large class with electrodes constructed of it impracticable. The initial expense is great and the care of it is a burden on the instructor.

In the Cornell laboratories, for ordinary work, graphite has been substituted. Trouble was experienced with this material on account of the fact that it was porous and absorbed the solutions in which it was used, and, therefore, could not be cleaned readily. This prevented its use in experiments where impurities might interfere with the desired reaction. Also, at high current densities the graphite electrodes showed a tendency to disintegrate and to fill the solution with clouds of finely divided graphite powder. This was due, possibly, to the discharge within its pores and beneath its surface of gases which forced off the surface particles. A further objection was found in the graphite's propensity for rubbing off and smutting.

After experimentation to determine a means of preventing the absorption of solutions by the graphite, it was found that if the graphite electrodes were treated while hot with molten paraffin, in amounts which are readily absorbed by them, the surface of the graphite acts as though it were greased, and is not wetted by aqueous solutions. Because of surface tension phenomena, the pores are not entered by the solutions. This treatment, by keeping solutions from the pores, should also prevent the disintegration of the electrodes at high current densities; however, whether it does or not has yet to be determined. Certainly it does not when the graphite is made anode in chloride solutions, but here we have the paraffin attacked by the evolved chlorine, and naturally its efficiency as a protective agent is diminished. The treatment with paraffin furthermore reduces to a minimum the inclination of the graphite to rub off, so that it is rendered quite clean and it may be handled freely without smutting.

When mention was made to the Acheson Graphite Company of the behaviour of the graphite thus treated, it was found that they had employed the same means for improving their electrodes when designed for certain purposes.

In the laboratory of Wesleyan University we are now using graphite electrodes made from Acheson sheet graphite of 0.5 cm. thickness. The sheet is cut into pieces which are 15 cm. by 2.5 cm. in dimensions. One end is copper plated, and a copper wire about 20 cm. long is twisted around this end and is soldered in place to the copper plate. To protect the exposed metal at this point from fumes, the end of the electrode is covered with a light coating of varnish. The graphite is then paraffined while hot. The electrodes are supported by a very simple device, which consists merely of a block of wood of sufficient size to rest across the top of a beaker. It contains two parallel slits, 2.75 cm. apart, and of the proper width to admit the electrodes and to hold them snugly in position.

We were thus enabled to supplant very satisfactorily by the use of paraffined graphite the platinum sheet electrodes heretofore used in ordinary experiments in laboratory work. In electrochemical analysis, however, and separations, expediency still demanded the use of the Classen platinum dish.

The use of a graphite dish as a substitute for the platinum dish need not be confined to pedagogic electrochemistry, but should also find an extended use in commercial laboratories.

Recent developments in the field of electrochemical analyses, due to the important work of Prof. E. F. Smith and his students, and other investigators, have afforded us many beautiful methods of electrochemical analysis which might well and should be used in industrial laboratories. This is especially true of those laboratories connected with metallurgical plants where some electrochemical methods are already in use. The substitution of the very rapid new methods for those already in vogue, requiring hours for precipitations and separations, which could be accomplished in a few minutes if accompanied by effective stirring, would perhaps recommend itself to the works chemist if this substitution could be made without the very considerable outlay now necessary for platinum electrodes. The very convenient Classen dish is not essential to the equipment requisite for electro-analysis, yet it is almost a necessity; one's equipment is scarcely complete without a number of them. To provide them, however, requires a considerable outlay.

By changing from the old system of electrochemical analysis to the new, a saving in the amount of platinum in use could undoubtedly be effected. The old system involves the use of the stationary, cylindrical, platinum cathodes, while the new methods depend on rotating electrodes, stirred solutions, the platinum dish, and other devices for making possible the use of high current densities. The only points that can be produced in favour of the stationary electrode method is that the electrolysis can be started in the late afternoon, and without further attention, may be allowed to complete itself during the night, and that the multiplication of the number of analyses does not involve an equal increment in the time required for the operation. However, increasing the number of analyses does increase the number of electrodes which are necessary, and therefore increases the cost for equipment. With a single rotating anode and Classen dish cathode, a number of analyses could be made with a time expenditure of only a few minutes for each analysis and would require the attention of only a fairly expert chemist.

In equipping a new laboratory for electrochemical analysis, it is clearly poor economy to instal the antiquated apparatus, the numerous stationary electrodes, in preference to the new, a much smaller number of rotating anodes and dish cathodes; and there are those who think, with reason, that it is also poor chemistry.

If our contention is true that it is both good economy and good analytical chemistry not only to equip laboratories with the apparatus requisite for performing rapid analyses in stirred solutions, but also, if necessary, to discard present equipment of stationary electrodes in order to do so, then much more true is our contention if an apparatus constructed of a much less expensive material than platinum can be offered the profession.

Anticipating these advantages and encouraged by the success of the paraffined graphite electrodes, a graphite dish was prepared from a four-inch cylindrical stick of Acheson graphite. This dish was turned out on a lathe by Mr. G. B. Upton, of Sibley College, Cornell University, for whose great kindness I take this opportunity of expressing my sincere appreciation.

Graphite was chosen as the material of which to construct the dish, because in it we have a substance which is at once a good conductor of the electric current, is cheap, is light in weight, and is non-attackable by solutions. Its density is low, a little less than 2.2 (Fitz-Gerald, *Trans. Am. Electrochem. Soc.*, 1907, xi.), but varies from one electrode to another and in different parts of a single electrode. With the density probably also varies the hardness, though the variation in both density and hardness is slight and gradual, so no difficulty on that account need be experienced in machining. Because of its low density, the walls of a dish may be made of sufficient thickness to lend strength and rigidity to the article without unduly increasing its weight.

The porosity of the graphite may prove to be the greatest obstacle in the way of the dish becoming a success when

* A Paper read at the Fifteenth General Meeting of the American Electrochemical Society, at Niagara Falls, Canada, May, 1909.

employed in the most accurate analysis. The degree of porosity is expressed numerically as the quotient obtained by dividing the difference between the real and apparent specific gravities by the real specific gravity (FitzGerald, *Ibid.*). The apparent specific gravity is that obtained when interstices of the graphite are kept free of the liquid in which the determination is being made. This is accomplished by coating the sample lightly with shellac. The real specific gravity is found after the air has been removed from the pores of the sample by greatly reducing the pressure over the immersing liquid. When the suction is released the evacuated pores become filled. The average of several determinations gives the porosity of graphite at about 0.25. Such a degree of porosity would seem to make this substance an impossible one of which to construct a dish designed for such purposes as is this one. The paraffin, however, is very effective in preventing the absorption of solutions into the pores. That the latter are not entirely filled by the paraffin is shown by the fact that alcohol is able to penetrate the paraffined graphite fairly readily. It is highly probable that while aqueous solutions do not enter the interstices, aqueous vapour does and condenses there to a certain extent; so it may be necessary eventually to fill these entirely with paraffin by the evacuation method used in the specific gravity determination.

The purity of graphite is high, and therefore it is improbable that any contamination of solutions can possibly result from its use. It has been shown (FitzGerald, *Journ. Frank. Inst.*, November, 1902) that when a carbonaceous substance, like anthracite coal, has been graphitised, its impurities are almost completely volatilised, the more complete being this volatilisation the higher the temperature of graphitisation and the longer the heat is maintained. This graphite is then a very pure form of carbon, and the Acheson product, in addition to its insolubility, has been shown to be very resistant to disintegration in solution (Foerster, *Zeit. Anorg. Chem.*, June, 1901). When made anode in caustic solutions it is only very slightly attacked by the evolved oxygen. This is to be expected when we recall that the combustion point of some forms of graphite in oxygen is about 600° C.

Graphite is to be had of varying degrees of hardness; the harder varieties, while less pure, are more resistant to chemical action and undoubtedly would make a stronger and more durable article. Hardness would likewise enhance the possibilities for accurate and sharp machining, a fact to be borne in mind when choosing a graphite for the purpose described in this paper.

Its tensile strength is about 80 per cent of that of the carbon from which it is made, there being a deterioration of 20 per cent in that property during the process of manufacture. With the combination of hardness and the above tensile strength, it is possible to machine a dish whose walls are of very slight and uniform thickness, which thus possesses both strength and lightness. The elasticity of the harder varieties of graphite is also worthy of note. Possessing these properties, there is no reason why a graphite dish with proper use should not prove to be long-lived to an entirely satisfactory extent.

The experimental dish was prepared for use by first burnishing on a revolving steel-wire buffer, which served to remove all dust and gave the surface a somewhat polished appearance. The graphite still rubbed off on the fingers, but to a much lessened extent; after treating with paraffin it no longer rubbed off at all.

The dish was warmed in a hot-air bath to a temperature of about 110°, and, while still hot, molten paraffin was applied with a brush until it was no longer absorbed readily, but remained visible on the surface. The dish was then returned to the oven, several sheets of filter-paper were placed under it, and the bath was maintained at the temperature of 110° for several hours. In this way the excess of paraffin was drawn off, by gravity and capillary action, into the filter-paper. After this treatment the surface of the graphite appeared quite dry. The dish was then re-burnished.

The preliminary experiments conducted with this dish gave such very promising results that two other dishes were obtained through the courtesy of Messrs. Eimer and Amend, of New York. These are much lighter in weight, weighing, respectively, 38 and 32 grms. after having been paraffined. Their capacity is 200 cc. In dimensions they are 9.5 cm. in diameter across the top and are 5 cm. deep. The lower part has the shape of a truncated cone, the conical shape beginning 2.5 cm. from the upper edge and extending inward at such an angle that a flat bottom of 3.5 cm. in diameter is afforded by the truncation. This shape was chosen so as to give a dish of straight sides. The walls are slightly less than 1 mm. in thickness. The interior of the dishes presents a surface area of 54 square centimetres.

Another dish has been designed which is hemispherical in shape, with the exception of a flattened portion of 3 cm. diameter on its bottom. Its dimensions are 9.5 cm. in diameter across the top and 4.5 cm. deep. The hemispherical shape has the advantage of affording the greatest capacity for the least wall area. As, of course, the weight of the dish lies in its walls, the smaller the area of the walls the less will be the weight. The hemispherical dish therefore gives the greatest capacity for the least weight.

The first experiments were made to determine the most satisfactory method for drying, attention being paid to speed as well as to accuracy. A method frequently used in drying the Classen dish with deposited metal is to work with absolute alcohol and to burn off the excess. Applying the severest test first, this method of drying was used; the dishes were washed with distilled water, followed by absolute alcohol, and the excess of alcohol was burnt off. After cooling in a desiccator the dishes were weighed.

Some of the results showed only a slight loss in weight, while others showed a loss of almost 5 mgrms., due, no doubt, as was found, to the loss in paraffin through being dissolved by the alcohol.

The method was then adopted of drying, after washing with distilled water, by holding the dishes by means of crucible tongs directly over the smokeless flame of a Bunsen burner, moving then around during the drying so that the heating would be uniform, and then cooling in a desiccator. This extremely crude method was justified by its rapidity and the surprisingly satisfactory results, as is shown by Table I.

TABLE I.

No.	Weight before. Grms.	Weight after. Grms.	Loss. Grms.
1.	37.2660	37.2660	None
2.	37.2660	37.2658	0.0002
3.	37.2658	37.2652	0.0006
4.	33.1400	33.1400	None
5.	33.1400	33.1400	"
6.	33.1400	33.1400	"

A number of determinations of efficiency was then made by electrolyzing an acidified solution of copper sulphate contained in a graphite dish in series with a copper coulometer filled with a portion of the same solution. Copper anodes were employed in both cells and a copper cathode in the coulometer. A current of 0.1—0.16 amperes was passed and the electrolysis was continued for about one hour in each run. Some of the results obtained are given in Table II.

TABLE II.

No.	Cathode gain in coulomb t.r. Grm.	Cathode gain in graphite dish. Grm.	Difference. Grm.
1.	0.1140	0.1128	-0.0012
2.	0.1582	0.1570	-0.0012
3.	0.1784	0.1770	-0.0014
4.	0.1748	0.1728	-0.0020
5.	0.2008	0.2004	-0.0004
6.	0.1924	0.1920	-0.0004
7.	0.1924	0.1924	-0.0000
8.	0.1772	0.1758	-0.0012
9.	0.1818	0.1802	-0.0016
10.	0.2126	0.2122	-0.0004

An occasional result failed signally to agree with the theoretical value. As a check on the method, a Classen dish, containing a similar solution and copper anode, was also placed in the circuit; this cell was worked in series with the other two. The platinum dish was dried with alcohol, the excess of which was burnt off, and was cooled in a desiccator. The results gotten with the Classen dish are shown in Table III.

TABLE III.

No.	Cathode gain in coulometer.	Cathode gain in Classen dish.	Difference.
	Grm.	Grm.	
1.	0.1140	0.1142	+0.0002
2.	0.1084	0.1040	-0.0044
3.	0.1748	0.1768	+0.0020
4.	0.2008	0.2030	+0.0022
5.	0.1924	0.1919	-0.0005
6.	0.1772	0.1753	-0.0019
7.	0.1818	0.1807	-0.0011

These results, as a whole, are hardly as good as those obtained with the graphite dish, and, like those, an occasional one was bad. The errors observed in the case of the Classen dish are doubtless due to hurried and perhaps careless manipulation. It may be noticed, moreover, that in the case of the graphite dish the results are mostly low, while in that of the platinum they are sometimes high and sometimes low.

In Table IV. the results obtained with the Classen dish are tabulated against those obtained with the graphite dish.

TABLE IV.

No.	Cathode gain in platinum dish.	Cathode gain in graphite dish.	Difference.
	Grm.	Grm.	
1.	0.1142	0.1128	-0.0014
2.	0.1040	0.1038	-0.0002
3.	0.1650	0.1642	-0.0008
4.	0.1768	0.1728	-0.0040
5.	0.2030	0.2031	+0.0001
6.	0.1919	0.1920	+0.0001
7.	0.1997	0.1974	-0.0023
8.	0.1753	0.1758	+0.0005
9.	0.1807	0.1802	-0.0005
10.	0.2125	0.2122	-0.0003

The results obtained for the graphite dish, as set forth in this table, are for the most part likewise lower than those obtained with the platinum dish. It appears that there is perhaps some loss in the weight of the dish itself in drying which causes the low results. Therefore, the method of drying directly over the flame will be abandoned, and instead the dishes will be washed thoroughly with distilled water and then dried rapidly in a stream of warm dry air.

The dishes are now being tested in actual analytical work. Known volumes of a standard copper solution are being analysed in them with rotating anode and at high current density. This will be considered a crucial test, and not until the results of this test are known can the dish be unqualifiedly recommended. This paper is therefore merely a preliminary note. No further tests are needed, however, we feel, to show that it may be substituted profitably in numerous electrochemical operations where the Classen dish has been employed heretofore, or would have been had it been a less expensive article.

These dishes have been suggested for use in other operations not connected with electrolysis, such as digestions in hydrofluoric acid at high temperatures. In such cases the beaker shape would probably be advantageous.

A rotating graphite anode has been designed to accompany the dishes. This is constructed after the general plan of the platinum anode described by Miss Langness (*Journ. Am. Chem. Soc.*, 1907, xxix., 459). It is dish-shaped and contains radial slits in its walls and a circular opening in its bottom. It is hoped that by means of it

the interesting results obtained with the anode referred to above may be duplicated.

Work is now being carried on, as intimated above, to show the limiting capabilities of the graphite cathode dish (manufactured and on sale by Eimer and Amend, New York). A further report, therefore, will be made. The efficacy of the dish in numerous electrochemical separations and operations will also be determined. It is also our intention to investigate the rotating dish anode referred to above, and a smaller disc-shaped rotating anode with a graphite stem.

Summary.

1. Simple graphite electrodes are described which are designed for use in the place of platinum as insoluble electrodes in electrochemical experiments.

2. An account is given of preliminary experiments with a graphite dish intended to supplant in some forms of electrochemical analysis the Classen platinum dish.

3. The dish is recommended for electrochemical separations and for analyses where great accuracy is not required. Confidence is felt that, after it has been further developed, it will be able to entirely take the place of the platinum cathode dish.

THE CHEMISTRY OF SYNTHETIC CAMPHOR.

By WILLIAM A. DARRAH, B.S.

THE list of those compounds for the supply of which commerce has been forced to rely upon nature is being rapidly shortened; perhaps the latest substance to be synthetically produced is camphor, which, while it is an article to be found in every household, has only recently been produced by manufacturing methods on a scale to successfully compete with the natural supply.

The term "synthetic" as applied to a chemical compound is commonly and most erroneously confused with "artificial"; though the difference is very great, particularly in the case of camphor. As correctly used the term "synthetic compound" is one produced by man though having exactly the same properties and constitution as the natural article. On the other hand, in the arts, the term "artificial" denotes an imitation of a natural product, which, while possessing some of the peculiarities of the substance from nature is yet essentially different.

This is well illustrated by the case of camphor, as it happens that the two terms are used in the camphor trade for different substances. As previously stated synthetic camphor is identical with common or Japan camphor, while artificial camphor, while resembling the natural in smell and general physical appearance, is chemically quite distinct. Thus Fig. 1 shows the formula of camphor, while the constitution of artificial camphor is given in Fig. 2.

With the view of analysing the development of the recent synthetic process, and to show the imperative need for such, it may be of interest to touch in a general way upon the occurrence and extraction of natural camphor. This is practically all derived from the juice of a tree closely related to our common laurel, but which grows to very much larger sizes. This tree, the *Larus camphora*, thrives best in the warm moist climates of southern China and Japan, from which part of the world the great portion of the natural supply is obtained. While the name common or "Japan camphor" discloses the largest producer, yet Java, Borneo, Sumatra, and the neighbouring islands are the source of a large part of the world's supply.

The natural process of extracting camphor is simplicity itself, and is as inefficient as it is simple. The substance occurs as small drops or "tears" disposed between the fibres of the wood, the root being particularly rich in camphor. The trees of Borneo and Sumatra contain comparatively large tears, which are extracted by the

natives after splitting the felled tree with crude wooden wedges. As thus obtained, the substance is fairly pure.

The trees of China and Japan, on the other hand, contain a larger number of much smaller deposits, more widely distributed, thus necessitating a more complicated process of extraction. The tree is first cut up into a number of small blocks or wedges about two inches upon a side, the faces being so chosen that the greatest amount of fibre end is exposed. To facilitate this the blocks are sometimes shredded.

Now camphor is very volatile at ordinary temperatures, it being one of those substances which at ordinary pressures will vaporise before melting. Therefore while the melting-point of camphor is twice that at which water boils, yet when the fibres of the camphor tree are heated in large vats of boiling water and the vapours are condensed, it is found that practically all of the camphor is removed, though in a very impure state. The preceding steps are usually carried out in Japan or China, where the trees abound and labour is cheap, while the final purification is done in Europe, Germany and England being the largest refiners.

Previous to transportation the camphor distillate is filtered through straw and brush matworks, which separate the flocculent camphor. The filtrate is pressed to exclude the excess of water, thus leaving the crude camphor in the

an analyser similar to the saccharometer used in the sugar industries. On comparing the rotary power of the specimen with a known standard from the same cake, the percentage of camphor may readily be determined.

As an ingredient in many patent medicines, as a preservative, and as the starting-point in the synthesis of numerous compounds, camphor has an enormous yearly consumption. Here is, therefore, the second powerful force acting toward the development of a synthetic process. Perhaps the determining cause, however, certainly an important factor in the situation, is the fact that the natural supply of camphor is monopolised by Japan, who naturally exacts a monopoly price for the product. These three causes combine to make the synthetic production of camphor profitable. First, the large and increasing demand; second, the limited supply; third, the present monopoly of the natural article. As a result synthetic camphor has recently been introduced, and is now being manufactured on a commercial scale.

The synthesis consists of six steps, but before entering upon the details it is of interest to trace the logical development of the process.

In making a survey of the possible sources from which camphor might be commercially synthesised several requirements must be kept in mind. The raw material must be cheap. It must be plentiful. It must be as closely related to camphor as possible, thereby reducing the amount of work required in the transformation to the minimum.

The compound which most nearly fits these requirements is pinene, which, as the chief constituent of turpentine oil, is both plentiful and cheap, while structurally it is closely allied to camphor. In fact, the closeness of this relation has led to previous attempts to devise a synthetic process. One notable instance of an unsuccessful trial was made at Ampere, N. J., and only failed after a determined effort to make a laboratory method commercial.

The first step in the procedure at present being used is the preparation of the pinene, by the fractional distillation of turpentine; that part which boils between 155° and 160° being 90 per cent pinene, which is the principal constituent of turpentine. The formula of this substance is shown in Fig. 3. It will be noted that it is double ring, aromatic, unsaturated hydrocarbon, closely related to camphor.

The distillate thus obtained is cooled and saturated with anhydrous hydrochloric acid, which transforms it from a clear transparent liquid to a white crystalline mass. This substance is pinene hydrochloride, known technically as artificial camphor, for reasons previously mentioned. It is interesting to note the shifting of the ring formation from that characteristic of pinene to that of camphene. The addition of the hydrochloric acid is therefore an expedient by means of which the ring formation is altered, and the double bond of unsaturation removed, for when, as in the next step, the acid is removed, not the original pinene but an isomer, camphene, is obtained. As shown graphically in Fig. 3 the structural formula is now more similar to camphor. It will be noted that the double bond, the point at which a compound is most open to attack, is now so placed that the addition of oxygen at the required point is a comparatively simple matter.

The removal of the hydrochloric acid may be accomplished by adding any substance having a stronger affinity for the acid than the pinene hydrochloride, and not possessing any radical to give in return. Three practical methods have been devised, namely:—

- (a). Heating with ammonia (NH₃), amines (NH₂), pyridine (C₅H₅N), or similar nitrogen compounds.
- (b). Heating NaOH, sodium hydrate, or a lead, sodium, or copper salt of a higher fat acid, as, for instance, soap.
- (c). Heating with an anhydrous acetate of sodium or lead in glacial acetic acid (CH₃COOH). The latter method gives the purest product.

Having removed the hydrochloric acid (see Fig. 3), the next step is to add on the necessary oxygen at the carbon atom next the double bond. Now it is almost impossible to

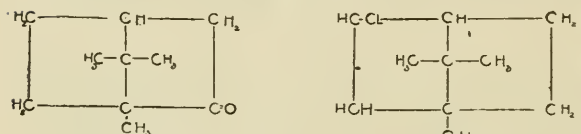


Fig. 1.

Fig. 2.

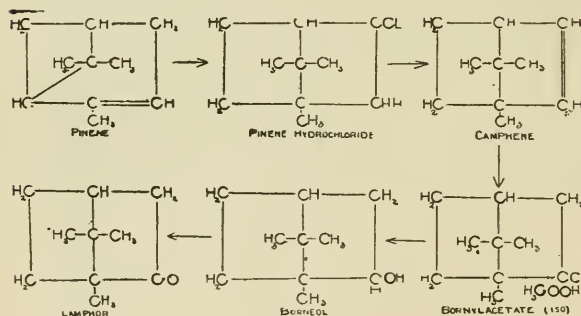


Fig. 3.

form of large impure cakes, in which shape it is exported. The further steps are the final purification, which consists essentially in fractional distillations, advantage being again taken of the ease with which the substance volatilises.

The most casual analysis of the above process reveals one of the inherent and insurmountable defects, namely, the whole tree is destroyed in the process of extraction. Now each tree yields on an average only 20 pounds of camphor, while it requires approximately thirty years in which to mature. It must be evident therefore that for this reason the natural supply of camphor is kept within very narrow limits, thus giving one very important stimulus to synthetic production.

The properties of camphor are so well known that it is scarcely necessary to name them here. It is a soft semi-transparent flaky substance with a characteristic smell. Common camphor is a dextro-rotatory, though both lævo and racemic types are known. Advantage was taken of the rotary effect of camphor upon polarised light in determining the amount of the pure substance in the crude cake as it comes from the Orient. A weighed amount, usually about 5 grms., is dissolved in a 98 per cent solution of ethyl alcohol. The solution is decanted and poured into

oxidise an organic compound directly without destroying the substance; however, some other radical may be first added, and an oxygen atom then substituted. This is the process followed in this case.

The camphene previously formed is dissolved in its own volume of glacial acetic acid, and 5 per cent of fuming hydrochloric acid added. The product thus formed is isobornyl acetate, an oil boiling at 225°, but, like camphor, volatile with steam. The structure is shown graphically in Fig. 3.

It now only remains to replace the acid radical by oxygen, and the process is complete. This is done in two steps. Since sodium hydrate has a stronger affinity for the acid than the isobornyl acetate, it might be expected that in the presence of this base the acetic acid would be separated; and such is the case. On adding a concentrated solution of sodium hydrate borneol is formed, and also a by-product of sodium acetate. A glance at the structure shows that when the OH or hydroxyl grouping of the borneol is replaced by oxygen, thus forming a ketone compound, the process is complete.

Such a secondary alcohol is readily oxidised, chlorine, oxygen, ozone, nitric acid, and a wide range of other oxidising substances being available. Chlorine is commonly employed in practice, and the yield, while not theoretical, is very satisfactory from a commercial standpoint. The product thus obtained is purified by sublimation, after which it is put upon the market. With two exceptions the synthesised product is identical with the natural. The exceptions are, first, the synthetic camphor is purer than the common variety, and, second, the laboratory camphor is of the racemic type (*i.e.*, it is not optically active), due to the fact that equal quantities of dextro- and laevo-rotatory camphor are produced.—*The Chemical Engineer*, 1909, ix., 163.

PROCEEDINGS OF SOCIETIES.

FARADAY SOCIETY.

Ordinary Meeting, June 29th, 1909.

Dr. N. T. M. WILSMORE in the Chair.

DR. HENRY J. S. SAND read a paper entitled "*Apparatus for the Rapid Electro-Analytical Separation of Metals.*"

The paper contains a description of some developments made in the apparatus, first described by the author about two years ago, for the rapid electro-analytical deposition and separation of metals (*Chem. Soc. Trans.*, 1907, xci., 373; also *Trans.*, 1908, xciii., 1572). This apparatus for the first time combined in a practical manner the use of an auxiliary electrode and very rapid stirring of the electrolyte, and made it possible, as has been shown so far, to deposit and separate from each other for purposes of chemical analysis the metals silver, mercury, copper, bismuth, lead, cadmium, zinc, antimony, and tin. The times required for these depositions varied in the majority of cases between five and fifteen minutes. Apart from the very high stirring efficiency of the electrodes the apparatus is believed to be superior to others of similar type in the exceedingly great simplicity of the method of making and undoing the electrical connections on a single stand, in the fact that the electrodes may be used with ordinary beakers, and in the simple manner in which the electrodes may be washed and dried. No alterations in principle have therefore been made to the apparatus, but the following additions and simplifications are described.

As hitherto, a mercury contact has been employed in the electrolytic stand to make the connection between the stationary and the moving parts; a special screw cap has, however, now been provided, which may be screwed down when the apparatus is not in use, making it possible to transport it without taking out the mercury.

A clutch arrangement has been added which enables the operator to start or stop the rotation of the anode without stopping the motor. Such an arrangement will be found of advantage if it is desired to actuate several sets of apparatus from one shaft driven by a single motor; or if the current is obtained from a small motor-generator which is also employed for rotating the electrode, the clutch making it possible to stop or start the stirrer without stopping the current; or lastly, if a hot air or water motor is employed which cannot be stopped instantly during the washing of the electrodes.

A very considerable simplification has been obtained by fitting all the apparatus required for the measurement of the potential of the electrode in a single box. The arrangement has been designed so that by depressing a key it will also allow the potential difference between the anode and the cathode to be read directly. It was thought very desirable to retain the capillary electrometer as a zero instrument, but it became necessary to design a new portable form suitable for the purpose in view. It may be described as a closed evacuated form developed from the Ostwald horizontal capillary electrometer. It is provided with an enclosed scale, and if observed by a lens of small magnification it will readily indicate 1 millivolt.

Dr. B. BECKETT DENISON communicated a paper entitled "*Researches on the Relative Rates of Migration of Ions in Aqueous Solution.*"

The author has determined by the method of direct observation of moving ionic boundaries the transport numbers of the halide salts of the metals of the alkalis and alkaline earths. The concentrations of the solutions were 0.1 to 0.02 normal. It is pointed out that the study of transport numbers by the direct and indirect methods has been shown to afford a means of determining the degree of hydration of the ions, although in the present paper no degrees of hydration were calculated.

Prof. R. ABEGG (communicated) congratulated the author on having succeeded in filling the gap of electro-chemical constants of so important a group of ions as the halides.

Mr. S. FIELD read in abstract a paper on "*The Conditions which determine the Composition of Electro-deposited Alloys. Part I. Copper-zinc Alloys.*"

As a result of a large number of experiments on the electrolytic deposition of brass, the author has, by the analysis of the deposits, shown the regular manner in which the composition changes with such varying conditions as (1) proportion of copper and zinc compounds in the solution; (2) strength of the solution; (3) temperature; (4) current density; and (5) the presence of free cyanide. It is thus shown that the proportion of zinc is increased (a) at lower temperatures; (b) with more dilute solutions; (c) with increased current density; and (d) by the absence of free cyanide. With a large proportion of zinc compound copper is still freely deposited. The author incidentally draws attention to a number of important conditions which primarily affect the composition of the solution, and ultimately the character and composition of the deposit. The work is being continued on other binary alloys.

NOTICES OF BOOKS.

Antimony. By CHUNG YU WANG, M.A., B.Sc. London: Charles Griffin and Co., Ltd. 1909.

This is the only book in the English language devoted exclusively to the preparation and uses of antimony, and contains considerably fuller details and more explicit information than can be found in the section on the metal in books on general metallurgy, or, indeed, anywhere except in the original papers which have been largely used in its preparation. New methods which are coming into general use are specially emphasised, such as the volatilisation process which is applicable to ores containing low percentages of antimony. After every chapter a biblio-

graphy is given, and for this alone the book will be of much assistance to the metallurgist. Every part of the book is thoroughly systematic, and great use is made of tabular schemes and classifications, which give a large amount of detailed information in a concise form. For instance, the extraction of the metal from its ores by various processes is tabulated in such a way as to show at a glance the outlines and essential points of the different processes.

Le Materia Radiante e I Raggi Magnetici. ("Radiant Matter and the Magnetic Rays"). By AUGUSTO RIGHI. Bologna: Nicola Zanichelli. 1909.

A SHORT account of recent research on radiant matter is given in this book, which is very lucidly written. Very little mathematics is introduced in the text, the formulæ relating to the motion of an electron in a uniform magnetic field, &c., being worked out in an appendix. Discharge in a magnetic field is treated comparatively fully, and the book gives an excellent short summary of the present state of our knowledge of radiant matter and magnetic rays.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlviii., No. 23, June 7, 1909.

Preparation of the three Oxy and of the *p*-Dimethyl-amido- and Diethylamido-benzylidene Camphors, and of the *p*- and *m*-Tolylidene Camphors.—A. Haller and Ed. Bauer.—The *o*, *m*, and *p*-oxybenzylidene camphors may be prepared by the condensation of the three oxaldehydes with camphor in presence of soda; *p*-dimethylamido and diethylamido benzylidene camphors are formed when the respective aldehydes are added in small quantities to an ethereal solution of camphor and soda, and the tolylidene derivatives similarly. The three oxy derivatives are colourless like benzylidene camphor itself, but their solutions in alkalis are more or less dark yellow. The specific rotatory power of these compounds in alcoholic solution is of the same order of magnitude as that of benzylidene camphor and the methoxybenzylidene camphors, though somewhat higher. The specific rotatory power increases as we pass from the meta and ortho to the para derivative. The specific rotatory power of the oxy derivative is higher when an alkaline solution is used. The dialkylamido derivatives are yellow, and give with acids, especially hydrochloric acid, colourless salts which are dissociated by water. These basic compounds have a much higher specific rotatory power than the oxy derivatives, and this power is much diminished by the addition of acids.

Chemical Reactions in Gaseous Mixtures subjected to very great Pressures.—E. Briner and A. Wroczynski. — Under very great pressure, and at the temperature of liquid air, the system NOHCl condenses to a dark red-violet solid which is undoubtedly an addition product. At the ordinary temperature this compound disappears, and the mixture becomes colourless, and after a time two layers of liquid appear, one light red and the other light yellow. The former is nitrosyl chloride, and the latter is water containing NOCl. The reaction occurs according to the equation $2\text{NO} + 2\text{HCl} = \text{NOCl} + \text{H}_2\text{O} + \frac{1}{2}\text{Cl}_2 + \frac{1}{2}\text{N}_2$. The system NO—SO₂ yields, under the same conditions, a pale green solid which is stable at the ordinary pressure and appears to be a mixed anhydride.

Hydrated Compounds of Thorium Chloride with Alkaline Chlorides.—Ed. Chauvenet.—The author has prepared the following double compounds of thorium and alkaline chlorides: ThCl₄.LiCl.8H₂O, ThCl₄.NaCl.10H₂O, ThCl₄.KCl.9H₂O, ThCl₄.2RbCl.9H₂O, ThCl₄.2CsCl.8H₂O, ThCl₄.2NH₄Cl.10H₂O. Thermic determinations show that the hydrates given by Li, Na, and K are more stable than those formed with Rb and Cs. The hydrates of the

chlorides of the three first metals are much less stable than the anhydrous chlorides, and much more stable as hydrates than those of the two last. Hence when the double hydrates of Li, Na, and K are dehydrated even in a current of hydrochloric acid a high temperature has to be used, and then the H₂O reacts to give oxyhaloids. Possibly at higher temperatures these oxyhaloids, Th(OH)Cl₃.MCl, would give ThOCl₂.LiCl, ThOCl₂.NaCl, ThOCl₂.KCl, and at a still higher temperature ThO₂ + ThCl₄ + 2LiCl, ThO₂ + ThCl₄ + 2NaCl, ThO₂ + ThCl₄ + 2KCl. This prediction has been verified for ThOHCl₃.LiCl.

Normal Butene and some Derivatives.—Georges Dupont.—Very good yields of normal butene can be obtained by dehydrating normal butyl alcohol with aluminium, absorbing the butylene by bromine, and decomposing the bromide by means of caustic potash at 180°. The volatile butene then distils over. Pure butene is a liquid which boils at 18.5°, and solidifies at -130°. With bromine it gives the dibromide, C₂H₅—CBr = CHBr, and a crystalline tetrabromide. From the cuprous derivative octadiene, C₂H₅—C≡C—C≡C—C₂H₅, can be prepared, and various syntheses can be effected by means of the magnesium derivative of butene bromide.

Synthesis of Derivatives of Racemic Fenone.—MM. Bouveault and Levallois.—The authors have previously described the preparation of an amide which has the composition of racemic dihydrofencholene amide, but has a lower melting-point. Hypobromite acts on dihydrofencholamide, a derivative of natural fenone, giving a symmetrical urea, diapofenchylurea, and with the racemic amide, obtained by mixing the two active amides, two symmetrical isomeric ureas are formed. The synthetic amide also gives two isomeric ureas. A mixture of two equal parts of the enantiomorphous ureas gives the racemic urea.

MISCELLANEOUS.

Series of Lectures on Scientific Microscopy.—These will be given at the Institute for Microscopy of the Jena University from October 11th to 16th, 1909. The microscopes and apparatus are lent for the occasion by Messrs. Carl Zeiss (Jena) Optical Works. The following is the syllabus of lectures, demonstrations, and practical lessons:—

October 11th—Dr. H. Ambronn: Lecture "On Abbe's Theory of the Formation of the Microscopic Image." Practical Lessons with the Diffraction Apparatus after Abbe.

October 12th—Dr. H. Ambronn: Lecture on "The Method of Testing Objective Systems." Practical Lessons with the Abbe Test Plate and the Abbe Apertometer.

October 13th—Dr. H. Siedentopf: Lecture on "Dark Ground Illumination." Practical Lessons in Dark Ground Illumination.

October 14th—Dr. A. Köhler: Lecture with Demonstration on Photomicrography. (a) Projection of the Image on the Plate. (b) Illumination of the Object with Transmitted and Incident Light. (Vertical Illuminator).

October 15th—Dr. A. Köhler: Lecture on "Photomicrography with Ultra Violet Light." Dr. H. Siedentopf: Lecture on "Ultramicroscopy."

October 16th—Demonstration relating to the Lectures delivered on the previous day. (a) "Photomicrography with Ultra Violet Light; (b) with Monochromatic Visible Light; (c) with Incident Light (Vertical Illuminator) for Metallography; (d) Ultramicroscopy of Firm Colloids; (e) Ultramicroscopy of Colloidal Solutions; (f) Ultramicroscopy of Cells and Fibres."

Application for admission to the above Course of Lectures should be sent to Herrn Dr. EHLERS, Beethovenstr. No. 14, Jena.

THE CHEMICAL NEWS

VOL C., No. 2592.

AN APPROXIMATE DETERMINATION OF THE BOILING-POINTS OF METALS.*

By H. C. GREENWOOD, M.Sc.,
Beyer Fellow of the University of Manchester.

(Concluded from p. 42).

Boiling-point Determinations of Metals which readily Carburise.

IN these cases very great difficulties were encountered which for long made it impossible to obtain even roughly concordant results. Numerous attempts were made to apply the magnesia tubes of the Berlin porcelain factory as crucible materials but even with very gradual heating they almost invariably cracked before the boiling-point of the metal had been reached. Eventually, after further fruitless efforts with magnesia and thoria, a method was devised to "brasque" carbon crucibles with highly shrunk pure magnesia,† although still many of the experiments proved failures owing to the breakdown of the lining. Only the results of these experiments in which the lining remained free from cracks, and in which none of the liquid metal had come in contact with the carbon, were considered suitable for the purpose in view. The graphite crucibles were 15 cm. long and 2.5 cm. internal diameter, a thick paste of the finely powdered magnesia, mixed with saturated magnesium chloride solution, was placed in the tube, and by means of a wooden former a uniform lining 2 mm. thick was obtained. After drying slowly at 200° C., the crucible was placed in the furnace, and the temperature gradually raised to about 1700° C., hydrogen chloride being given off copiously during the process. It was found that the minimum risk of the brasque cracking was secured by adding the charge of metal, after allowing the crucible only to cool to about 1300° C., the experiment being performed immediately afterwards. The magnesia brasques prepared in this manner remained perfectly hard and coherent after heating to 1800° C., and even when subjected to 2500° C. Some trouble is caused by the fact that at about 1700° C. the magnesia begins to react with carbon, giving a dark grey sublimate. This action is, however, not sufficiently vigorous to seriously interfere with the observation of the metal, except, perhaps, at the high ebullition temperature of iron.

Aluminium.—Deville stated that aluminium was not volatile at a white heat, and recently Wartenberg has estimated that the boiling-point lies above 2200° C. In consideration of the facility with which this metal vaporises *in vacuo*, and also from observations on its behaviour in the electric furnace, it was suspected that this value was considerably too high.

In addition to its great affinity for carbon, another difficulty encountered with aluminium is the tenacious surface film of oxide which always covers the molten metal.

On gradually raising the temperature of the brasqued crucible with its charge of aluminium (about 3 cm. deep), there is no visible motion of the surface of the metal, and no marked sublimation until 1700° is reached. At 1790°, as read on the outside of the crucible, a sudden very vigorous agitation of the surface is observed; in some cases the metal frothed right up the crucible, and globules of metal were ejected very freely from the top of the crucible, a marked noise being also noticed.

To estimate the error due to the low thermal conductivity of the lining, the boiling-points of silver and copper were

determined under similar conditions in brasqued crucibles. The values obtained, however, were practically the same as those indicated above, so that no correction appears to be necessary. We may therefore fix the boiling-point of aluminium as approximately 1800°. The metallic residue in the crucible, in all experiments which gave a definite indication of ebullition, was found to be only very slightly carburised.

How greatly carburisation affects the ebullition can be judged from the fact that aluminium heated in an unbrasqued graphite crucible to 2100° shows not the slightest sign of boiling.

Manganese.—The difficulties in this case were even greater than with aluminium, on account both of the higher temperature of vaporisation and of the marked corrosive action of the metal upon the magnesia brasque. Consequently only a few of the numerous experiments proved successful.

The metal employed was Merck's "extra pure" fused manganese, which was found to be free from aluminium. The different stages of the boiling were quite clearly defined owing to the absence of any surface film. A slight agitation of the surface was apparent at 1850°, ebullition at 1900°, and at 1950° the metal vapour was burning at the top of the crucible with a large yellowish flame.

The boiling-point may be given approximately at 1900°. In an unbrasqued crucible no marked vaporisation of the metal was obtained at 2200°, thus showing the great effect of carburisation.

First gentle agitation of surface.	Decided ebullition.	Very vigorous ebullition.
1850°	1875°	—
1850	1900	—
1860	1890	1925°

Chromium. In this case also the brasque is to some extent acted upon by the metal, but fairly definite observations could be made, showing the agitation of the surface to commence at about 2175° and boiling at about 2250°. In an unbrasqued crucible no marked volatilisation is observed at 2500°.

Magnesium.—Until recently the measurement of Ditté (*Comptes Rendus*, 1871, lxxiii., 108), who found the boiling-point to be 1100°, has not been seriously thrown in doubt, but Wartenberg's (*loc. cit.*) published result group magnesium with copper, tin, and aluminium, with boiling-point above 2200°. It is difficult to see to what this uncertainty is due. In a graphite crucible, steady ebullition is clearly visible at 1000°, and measurements made with a protected thermo-element immersed in the molten metal indicate a well defined constancy of temperature for some minutes about 1120°, the metal distilling off. There seems little reason, therefore, for classing magnesium with metals of high boiling point.

Iron.—With iron of 99.9 per cent purity, ebullition was found to set in at about 2450°. Observations of the surface were rendered difficult by the products of the reaction between the magnesia and carbon, which at this high temperature is very vigorous. The carbon content of the metal after the experiments was under 0.1 per cent.

Conclusion.

Subject to the corrections which may be necessary when the temperature scale has been more accurately fixed, the following approximate measurements may be given of the boiling-points as determined in the present investigation:—

Aluminium	1800°
Antimony	1440
Bismuth	1420
Chromium	2200
Copper	2310
Iron	2450
Lead	1525
Magnesium	1120
Manganese	1900
Silver	1935
Tin	2270

* A Paper read before the Royal Society, May 27, 1909.

† Prepared by heating pure calcined magnesia, packed around a carbon rod maintained at high temperature by passing through the rod an electric current.

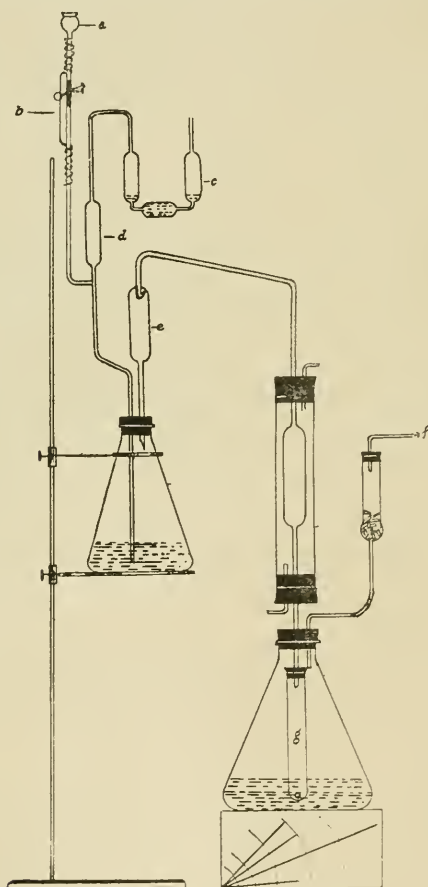
Some of the incidental expenses of this research have been borne out of the funds provided by the Government Grant Committee of the Royal Society. I wish to express my indebtedness to Dr. R. S. Hutton for his continual interest and advice during the progress of the work.

MODIFIED APPARATUS FOR ESTIMATION OF NITROGEN BY THE KJELDAHL PROCESS.

By F. E. WESTON, B.Sc., and H. R. ELLIS, B.Sc.

IN distilling off the NH_3 in a Kjeldahl estimation the above modified form of apparatus was employed. After diluting the HSO_4 with water and cooling, NaOH solution was run in through the thistle funnel *a*, which was supported by a stout copper wire. The bulb (about 10 cc.) *d* was to prevent any caustic soda solution from coming in contact with the strong H_2SO_4 in bulbs *c*.

The bulbs *c* were used to prevent any NH_3 from entering the apparatus when air was drawn through; the two side



a. Thistle funnel, rubber, and clips. *b.* Stout copper wire for supporting the thistle funnel. *c.* Bulbs for strong H_2SO_4 . *d.* Safety bulb. *e.* Trap. *f.* Bulb containing broken glass, connected to a pump. *g.* Test-tube with a small hole at the bottom.

bulbs were about 6 cc. in capacity, and the middle one 2 to 3 cc. The trap *c* was to prevent any solid matter being carried over during the distillation; the volume of the bulb was 15 to 20 cc.

During the distillation a steady current of air was drawn

through the apparatus; this enabled the distillation to proceed very smoothly, with absolutely no pumping, and very little attention was required.

The Polytechnic, Regent Street, W.

THE GRAVIMETRIC DETERMINATION OF SILVER AS THE CHROMATE.

By F. A. GOOCH and ROWLAND S. BOSWORTH.

IT has been shown in a recent paper from the Kent Chemical Laboratory of Yale University (Gooch and Weed, *Am. Journ. Sci.*, 1908, xxvi., 85) that the precipitation of silver chromate from the solution of a soluble chromate made faintly acid with acetic acid may be carried to completion by the addition of silver nitrate in considerable excess; and that the exact determination of the chromium of a soluble chromate or dichromate may be effected by treating with silver nitrate the solution of either salt, adding ammonia to alkalinity and then acetic acid to faint acidity, transferring the precipitate and washing it in the filtering crucible with a dilute solution of silver nitrate until foreign material other than that reagent has been removed, finishing the washing with a small amount of water applied judiciously in portions, and weighing the dried or gently ignited residue of silver chromate. The success of this process turns upon keeping the chromium at the moment of precipitation essentially in the form of chromate rather than dichromate, and in taking care that an excess of silver nitrate shall be present nearly to the end of the washing. The present paper deals with the conditions under which, in reversal of the process just described, silver may be precipitated completely as the chromate.

In the first experiments to be described, a solution of potassium dichromate was added gradually, either in slight excess or in considerable excess, to a solution of silver nitrate maintained at the boiling-point; the mixture was cooled and treated with ammonia until the precipitate first formed had been dissolved; acetic acid was added to faint acidity; and the precipitate was settled for half-an-hour, filtered off on asbestos in a perforated crucible, washed with a little water, dried, and weighed. In every case the weight of silver chromate found was deficient, and the testing of the filtrate with hydrochloric acid showed the presence of a soluble salt of silver. The errors amounted to several mgrms., varying with the conditions. Dilution of the original solution and prolonged washing with water increased the error. Admixture of alcohol was without appreciable effect upon the solubility of the precipitate. Evaporation to dryness and transfer by a dilute solution of potassium dichromate, and a final washing with water used judiciously in small portions, tended to diminish the amount of soluble salt, but this treatment never reduced the error of loss below two or three mgrms. for volumes approximating a hundred cubic centimetres. Solution of the first precipitate in ammonia and re-precipitation by boiling to low volume to remove the excess of ammonia failed to overcome entirely the solubility of the silver salt, which appears to be due to a tendency on the part of the ammonium chromate to pass to the condition of dichromate with loss of ammonia from the boiling solution.

In the next experiments, therefore, potassium chromate was used as the precipitant. In Table I., A, are given the details of experiments in which an excess of potassium chromate was added to silver nitrate, the solution boiled, the precipitate transferred to the asbestos filter in a perforated crucible by means of a dilute solution of potassium chromate, and washed with small portions of water, and the residue, after drying with gentle heat, weighed as silver chromate. In these experiments no silver was found in the filtrate, but the precipitate was not so coarsely crystalline and easily washed as when deposited by removal of

ammonia from an ammoniacal solution. In the other experiments of Table I., therefore, the first precipitate was dissolved in ammonia and re-precipitated by boiling the solution; in those of B the evaporation was carried to dryness, and in those of C the concentration was stopped when a volume of 10 to 15 cc. had been reached. In all these experiments precipitation was complete, the filtrates giving no test with hydrochloric acid for a dissolved silver salt.

TABLE I.

Silver taken as AgNO ₃ .		K ₂ CrO ₄ used.		Ag ₂ CrO ₄ weighed.	Silver found.	Error in terms of silver.
Volume of solution. Cc.	Weight of silver. Grm.	Volume of solution. Cc.	Weight. Grm.	Grm.	Grm.	Grm.
A.—Precipitation by K ₂ CrO ₄ .						
15	0.1652	50	0.3	0.2536	0.1649	-0.0003
10	0.1101	50	0.3	0.1693	0.1101	—
25	0.1437	50	0.3	0.2200	0.1436	-0.0001
25	0.1437	50	0.3	0.2210	0.1437	—
B.—Precipitation by K ₂ CrO ₄ , Treatment with NH ₄ OH, and Evaporation to Dryness.						
25	0.1348	50	0.3	0.2077	0.1351	+0.0003
30	0.1618	50	0.3	0.2500	0.1626	+0.0008
30	0.1618	50	0.3	0.2520	0.1639	+0.0021
C.—Precipitation by K ₂ CrO ₄ , Treatment with NH ₄ OH, and Boiling to a Volume of 10 to 15 cc.						
25	0.1576	50	0.3	0.2422	0.1575	-0.0001
25	0.1576	50	0.3	0.2414	0.1570	-0.0006
50	0.3152	50	0.3	0.4852	0.3155	+0.0003
50	0.3152	50	0.3	0.4843	0.3149	-0.0003
50	0.3152	50	0.3	0.4847	0.3152	—
D.—Precipitation by K ₂ CrO ₄ , Treatment with NH ₄ OH, and Boiling to a Volume of 10 to 15 cc. in presence of 1 gm. of Sodium Nitrate.						
10	0.1101	50	0.3	0.1693	0.1101	—
15	0.1652	50	0.3	0.2536	0.1649	-0.0003

once, or by dissolving the precipitate* in ammonia, re-precipitating by boiling to a volume of 10 to 15 cc., and then filtering, drying, and weighing.

In many cases it is desirable to determine silver present in solutions containing free nitric acid. The effect of free nitric acid upon the process was therefore next studied. A few qualitative experiments showed that the solvent action of nitric acid may be obviated by taking care to use the precipitant, potassium chromate, in such amounts that an excess of it shall be present after taking up the nitric acid to form potassium dichromate. The details of a few of these experiments are given in Table II.

TABLE II.

Ag in AgNO ₃ .		To form Ag ₂ CrO ₄ .		To form K ₂ Cr ₂ O ₇ with HNO ₃ .		Theoretically required.	Present.	Ag in filtrate.
Grm.	Grm.	Grm.	Grm.	Grm.	Grm.	Grm.	Grm.	Grm.
0.1376	0.063	0.1241	0.1946	0.1946	0.3187	0.3172	Found	
0.1376	0.063	0.1241	0.1946	0.1946	0.3187	0.3172	Found	
0.0550	0.063	0.0496	0.1946	0.1946	0.2442	0.3172	None	
0.0550	0.063	0.0496	0.1946	0.1946	0.2442	0.3172	None	
0.1376	0.063	0.1241	0.1946	0.1946	0.3187	0.3806	None	
0.1376	0.063	0.1241	0.1946	0.1946	0.3187	0.4758	None	
0.1376	0.095	0.1241	0.2919	0.2919	0.4160	0.4758	None	
0.1376	0.126	0.1241	0.3892	0.3892	0.5133	0.6344	None	
0.1376	0.158	0.1241	0.4865	0.4865	0.6106	0.7930	None	

In Table III. are given the results of quantitative experiments in which precipitation was effected in presence of nitric acid, with care to insure the necessary excess of potassium chromate. In the experiments of A the precipitate was filtered off at once, without solution by ammonia and re-precipitation by boiling; in those of B the ammonia treatment was made to convert the less crystalline precipitate to better form for filtration and washing.

So it appears that from solutions of silver nitrate, containing free nitric acid, potassium chromate precipitates silver chromate completely, provided enough potassium

TABLE III.

Silver taken as AgNO ₃ .		K ₂ CrO ₄ used.		HNO ₃ .		Ag ₂ CrO ₄ weighed.	Silver found.	Error in terms of silver.
Volume of solution. Cc.	Weight. Grm.	Volume of solution. Cc.	Weight. Grm.	Volume. Cc.	Weight. Grm.	Grm.	Grm.	Grm.
A.—Precipitation by K ₂ CrO ₄ in presence of HNO ₃ .								
25	0.1355	50	0.9	10	0.182	0.2091	0.1360	+0.0005
25	0.1355	50	0.9	10	0.182	0.2081	0.1353	-0.0002
25	0.1358	50	0.9	10	0.182	0.2090	0.1360	+0.0005
25	0.1355	50	0.9	10	0.182	0.2075	0.1349	-0.0006
25	0.1355	50	0.9	10	0.182	0.2090	0.1360	+0.0005
B.—Precipitation by K ₂ CrO ₄ in presence of HNO ₃ , Treatment with NH ₄ OH, and Boiling to a Volume of 10 to 15 cc.								
25	0.1348	50	0.6	10	0.063	0.2076	0.1350	+0.0002
25	0.1348	50	0.6	10	0.063	0.2068	0.1344	-0.0004
25	0.1348	50	0.6	10	0.063	0.2072	0.1347	-0.0001
25	0.1348	50	0.6	10	0.063	0.2074	0.1348	—
25	0.1348	50	0.6	10	0.063	0.2070	0.1346	-0.0002

The high results obtained in the experiments of B are no doubt due to the inclusion of foreign matter in the silver chromate, which is left in caked condition by the process of complete evaporation. The better results in the experiments of C are apparently due to the fact that in them the evaporation was not pushed too far. The experiments of D show that the presence of a gm. of sodium nitrate has no appreciable effect upon the solubility of the silver chromate. It is plain that the precipitation by potassium chromate in neutral solution is practically complete, and that accurate determinations may be made by filtering at

chromate is present to take up the nitric acid with formation of potassium dichromate as well as to form the silver salt. The precipitate, filtered at once or brought to better crystalline condition by treatment with ammonia and boiling of the solution to small volume, may be transferred to the asbestos filter by dilute potassium chromate and washed by small portions of water without appreciable loss. The weight of the residue of silver chromate, dried at gentle heat, may be taken as a very fair measure of the silver originally present.—*American Journal of Science* vol. xxvii, March, 1909.

SODIUM ALUM.

By WARREN RUFUS SMITH.

SODIUM alum, $\text{Na}_2\text{SO}_4\text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$, was made by several of the earlier observers, but its existence has been questioned several times. One of the latest to deny the existence of this compound is Ostwald, who says that the potassium in ordinary alum may be replaced by cesium or rubidium, but not by sodium or lithium ("Principles of Inorganic Chemistry," trans. by Findlay, p. 565). On the other hand, Auge (*Comptes Rendus*, cx., 1139) and Wadmore (*Proc. Chem. Soc.*, xxi., 150) have affirmed the existence of sodium alum. No one, however, has applied any criterion, other than analysis, to prove or disprove the existence of sodium alum as a definite chemical species. The experiments described below show that sodium and aluminium sulphates crystallise together, that the double salt formed is a chemical species, and that it is a true alum.

Whenever approximately equivalent amounts of sodium and aluminium sulphates are dissolved in water and made to crystallise at ordinary temperatures, octahedral crystals are obtained which, as shown by the analyses below, correspond in composition with the theoretical sodium alum. The best method of manufacturing this compound is to dissolve the materials in an amount of water sufficient to give a solution moderately supersaturated at ordinary temperatures, and then cool the solution and induce crystallisation by stirring or by seeding. Small crystals will be obtained similar to "alum meal." If larger crystals are desired, they can be made by slow evaporation at ordinary temperatures. That this substance is a definite chemical species is proved by the fact that the composition does not vary when crystallised from solutions of varying composition. The first of the analyses below is that of material from a solution containing the two sulphates in equivalent proportions; the second, of material from a solution containing sodium sulphate in excess.

	Calculated.	Found.	
		I.	II.
Na.. ..	5.03	5.12	5.18
Al.. ..	5.91	5.99	6.07
SO_4	41.90	42.45	41.94
H_2O	47.16	46.69	46.90

If the solution is made so strong that crystallisation starts at a temperature much above 30° , instead of clear crystals of the alum, a mass of small crystals of aluminium sulphate is obtained. If these crystals are kept in contact with their mother-liquor at laboratory temperatures for some time, crystals of sodium alum will appear, and, after some weeks, the entire mass will be changed to well-formed crystals of the alum. A quantity of material which separated from a warm solution was filtered off, dried between filter-papers, and analysed, giving figures corresponding closely to aluminium sulphate with 16 per cent anhydrous sodium sulphate. Other analyses of material obtained in a similar way gave similar figures varying more or less from the above proportion, showing that the mass is simply aluminium sulphate contaminated with sodium sulphate from the mother-liquor. If sodium alum is kept in contact with its saturated solution at temperatures above about 30° , it is decomposed into an opaque finely divided mass which is probably aluminium sulphate. The exact temperature of the transition has not yet been determined. Some of these phenomena have been noted by other observers, but their true explanation has not been given. The reason why the existence of sodium alum has been questioned probably lies in the fact that it is not formed at temperatures much above 30° . Attempts to prepare sodium chromium alum, sodium iron alum, and lithium aluminium alum by methods similar to those which give sodium aluminium alum were unsuccessful.

That sodium alum is a true alum is shown by the fac

that it forms mixed and layer crystals with other alums. With ordinary potash alum such mixtures are not very easily obtained, probably on account of their different solubilities. However, after repeated trials, a quantity of material was obtained, a single crystal of which contained potassium and sodium in the ratio of four to one. On the other hand, sodium alum readily forms layer crystals with chrome alum.

The solubility of sodium alum is given below. These figures were obtained as follows:—A quantity of the salt and a quantity of water insufficient to dissolve it were placed in one bottle, in another was placed a quantity of the salt and a quantity of its solution saturated at a temperature higher than that at which the observation was to be made. These bottles were stoppered and rotated for about six hours in a bath, the temperature of which was constant to within about 0.04° . This bath was controlled by a thermostat similar to one described by Magnusson, which was found to be efficient under trying conditions (*Journ. Phys. Chem.*, xi., 21). After rotation, about 10 cc. of solution were withdrawn from each bottle by a pipette, transferred to a platinum dish, weighed, evaporated to dryness, and the residue heated to constant weight at 250° . On evaporating these solutions to dryness at a temperature below 100° , in several instances a perfectly clear amorphous glassy residue was left, which on further heating gave an opaque mass like "burnt alum." This amorphous residue could be nothing but a solid solution of the two sulphates and water, as a specimen of it was found to contain about 30 per cent water.

Grms. Anhydrous Material contained in 100 Grms. Solution.

	From unsaturated solution.	From supersaturated solution.	Average.
10°	26.86	27.27	26.9
15°	27.87	28.00	27.9
20°	29.06	28.98	29.0
25°	30.13	30.13	30.1
30°	31.49	31.43	31.4

Grms. $\text{Na}_2\text{SO}_4\text{Al}_2(\text{SO}_4)_3$ per 100 Grms.

	Water.	Solution.
10°	36.7	26.9
15°	38.7	27.9
20°	40.9	29.0
25°	43.1	30.1
30°	45.8	31.4

Grms. $\text{Na}_2\text{SO}_4\text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ per 100 Grms.

10°	103.1	50.8
15°	111.3	52.7
20°	121.4	54.8
25°	131.8	56.9
30°	146.3	59.4

—*Journal of the American Chemical Society*, xxxi., No. 2.

SOME ORGANIC TUNGSTATES.

By JOHN B. EKELEY.

FRESHLY prepared tungstic acid, H_2WO_4 , dissolves readily in aqueous solutions of most aliphatic amines, with the formation of substituted ammonium tungstates. From the resulting solutions the salts crystallise out on evaporation, except in some cases where it is first necessary to evaporate to dryness, drive off the excess of amine at about 105° , and then crystallise. Of the salts described in this paper, all but two are readily soluble in water. Ethylenediammonium tungstate is difficultly soluble after it has once crystallised out. Diamylammonium tungstate dissolves with difficulty in water, but readily in methyl alcohol.

If any of these salts are heated slowly, the amine is driven off and at the same time the tungstic acid is partially reduced to the blue oxide, which, on further heating, glows and quickly changes to the yellow WO_3 .

In all cases the tungstic acid was prepared by boiling finely powdered sodium tungstate with concentrated hydrochloric acid, and washing the yellow precipitate by decantation until free from chlorides. Salts of the following bases were prepared:—Methylamine, dimethylamine, trimethylamine, ethylamine, diethylamine, propylamine, dipropylamine, diamylamine, and ethylenediamine. The water of crystallisation in the salts was determined by drying at 110° to constant weight, and the WO_3 by heating to constant weight at a low redness.

Methylammonium Tungstate, $(\text{CH}_3\text{NH}_2)_6\text{W}_7\text{O}_{24}\cdot 6\text{H}_2\text{O}$.

Tungstic acid was dissolved in a slight excess of 33½ per cent methylamine solution, evaporated to dryness on the water-bath, heated at 105° until there was no odour of methylamine, dissolved in water, and re-crystallised. Colourless prisms, which begin to lose their water of crystallisation as soon as they are dry.

$(\text{CH}_3\text{NH}_2)_6\text{W}_7\text{O}_{24}\cdot 6\text{H}_2\text{O}$.—Calculated — H_2O , 5.46; WO_3 , 82.34. Found— H_2O , 5.10; WO_3 , 82.38.

Dimethylammonium Tungstate,

$[(\text{CH}_3)_2\text{NH}]_{10}\text{W}_{12}\text{O}_{41}\cdot 13\text{H}_2\text{O}$.

Tungstic acid was dissolved in a slight excess of 33½ per cent dimethylamine solution, evaporated on the water-bath, and allowed to crystallise. Colourless truncated octahedra, which retain their water of crystallisation fairly well.

$[(\text{CH}_3)_2\text{NH}]_{10}\text{W}_{12}\text{O}_{41}\cdot 13\text{H}_2\text{O}$. — Calculated — H_2O , 6.58; WO_3 , 78.34. Found— H_2O , 6.66; WO_3 , 78.28.

Trimethylammonium Tungstate,

$(\text{CH}_3)_3\text{N}]_2\text{W}_4\text{O}_{13}\cdot \text{H}_2\text{O}$.

Tungstic acid was dissolved in a slight excess of a 33½ per cent trimethylamine solution, evaporated on the water-bath, and allowed to crystallise. Colourless needles and plates.

$[(\text{CH}_3)_3\text{N}]_2\text{W}_4\text{O}_{13}\cdot \text{H}_2\text{O}$. — Calculated — H_2O , 1.65; WO_3 , 85.76. Found— H_2O , 1.50; WO_3 , 85.61.

Ethylammonium Tungstate, $(\text{C}_2\text{H}_5\text{NH}_2)_6\text{W}_7\text{O}_{24}\cdot 5\text{H}_2\text{O}$.

Tungstic acid was treated with a slight excess of 33½ per cent ethylamine solution, and allowed to evaporate spontaneously. Colourless prisms were obtained, which do not lose their water of crystallisation so easily as the corresponding salt from methylamine.

$(\text{C}_2\text{H}_5\text{NH}_2)_6\text{W}_7\text{O}_{24}\cdot 5\text{H}_2\text{O}$. — Calculated — H_2O , 4.40; WO_3 , 79.68. Found— H_2O , 4.38; WO_3 , 80.04.

Diethylammonium Tungstate,

$[(\text{C}_2\text{H}_5)_2\text{NH}]_2\text{W}_4\text{O}_{13}\cdot 3\text{H}_2\text{O}$.

Tungstic acid was treated with diethylamine and water and warmed. After the solution had stood a day a white residue was filtered off. The filtrate was partially evaporated on the water-bath, and then allowed to evaporate spontaneously. After several days the liquid became thick, showing a few minute crystals throughout the mass. The colloid could be drawn out into threads. The whole mass was then evaporated again on the water-bath, but it held moisture tenaciously. On drying at 105° until there was no further odour of the amine, the mass became brittle. It was dissolved in water and allowed to stand. After a day, large pale straw-coloured crystals formed, which become opaque shortly after being removed from the mother-liquor. The crystals are truncated octahedra and prisms, which, when dry, melt to a viscous blue liquid on being heated.

$[(\text{C}_2\text{H}_5)_2\text{NH}]_2\text{W}_4\text{O}_{13}\cdot 3\text{H}_2\text{O}$.—Calculated— H_2O , 4.79; WO_3 , 79.94. Found— H_2O , 4.71; WO_3 , 80.39.

Propylammonium Tungstate, $(\text{C}_3\text{H}_7\text{NH}_2)_{10}\text{W}_{12}\text{O}_{41}\cdot 6\text{H}_2\text{O}$.

Tungstic acid was warmed with propylamine and water, evaporated on the water-bath, and allowed to crystallise. Minute colourless needles.

$(\text{C}_3\text{H}_7\text{NH}_2)_{10}\text{W}_{12}\text{O}_{41}\cdot 6\text{H}_2\text{O}$.—Calculated— H_2O , 3.02; WO_3 , 77.91. Found— H_2O , 2.96; WO_3 , 77.97.

Dipropylammonium Tungstate,

$[(\text{C}_3\text{H}_7)_2\text{NH}]_2\text{W}_4\text{O}_{13}\cdot \text{H}_2\text{O}$.

Tungstic acid dissolves slowly in dipropylamine and water. The solution was evaporated to dryness on the water-bath, the residue heated several hours at 105° , and re-crystallised from water. Colourless hexagonal plates and short thick prisms, having an appreciable purple colour in thick layers, melt on heating to a blue liquid, giving off amine.

$[(\text{C}_3\text{H}_7)_2\text{NH}]_2\text{W}_4\text{O}_{13}\cdot \text{H}_2\text{O}$.—Calculated— H_2O , 1.54; WO_3 , 79.60. Found— H_2O , 1.33; WO_3 , 79.59.

Diamylammonium Tungstate,

$[(\text{C}_5\text{H}_{11})_2\text{NH}]_2\text{W}_5\text{O}_{16}$ (anhydrous).

Tungstic acid, on being treated with diamylamine and water, partly dissolves and partly forms a white sticky mass. This was evaporated on the water-bath to dryness, and then heated at about 110° until most of the amine odour had disappeared. The residue is only slightly soluble in water, but dissolves in methyl alcohol to a pale straw-coloured solution, from which, after standing several days, long pale straw-coloured needles (sometimes several inches in length and about a square millimetre in cross section) separate. On removing the transparent needles from the mother-liquor, they quickly become opaque, losing alcohol of crystallisation. It was impossible to obtain checking results as to how much alcohol of crystallisation the crystals contained.

$[(\text{C}_5\text{H}_{11})_2\text{NH}]_2\text{W}_5\text{O}_{16}$. — Calculated — WO_3 , 77.74. Found— WO_3 , 77.66.

Ethylenediammonium Tungstate, $\text{C}_2\text{H}_{10}\text{N}_2\text{W}_2\text{O}_7$.

Tungstic acid was dissolved in a slight excess of ethylenediamine solution and heated on the water-bath. As the solution increased in concentration white microscopic needles separated, which were soluble in water with difficulty. They contained water of crystallisation, but no checking results were obtained in the moisture determinations.

$\text{C}_2\text{H}_{10}\text{N}_2\text{W}_2\text{O}_7$.—Calculated WO_3 , 85.61. Found — WO_3 , 85.97.

—*Journal of the American Chemical Society*, xxxi., No. 6.

THE SEPARATION OF TIN AND ANTIMONY.*

By LEROY W. McCAY.

THE action of hydrogen sulphide on hydrofluoric acid solutions of arsenic, antimony, tin, and other heavy metals has been studied by Arthur A. Noyes ("A System of Qualitative Analysis, including nearly all the Metallic Elements," Part II.; *Tech. Quart.*, 1904, xvii., 214). He found that although hydrogen sulphide has no action on a solution of stannic fluoride containing free hydrofluoric acid, it does precipitate antimony partially from a similar solution of antimony fluoride. He says nothing about the action of the gas on hydrofluoric acid solutions of arsenic, antimony, and tin, when these elements are present in their different states of oxidation. His experimental work led him to conclude that it is not possible to separate quantitatively tin and antimony in hydrofluoric acid solution with hydrogen sulphide. My experimental work goes to show that when the hydrofluoric acid solution contains all the

* From *Journal of the American Chemical Society*, xxxi., No. 3.

tin in the stannic, and all the antimony in the antimonious state, it is possible, by a proper regulation of the conditions, to separate the two elements quantitatively with hydrogen sulphide.

When a current of hydrogen sulphide is passed into (1) a moderately dilute solution of antimonious fluoride, containing some free hydrofluoric acid, or into (2) a moderately dilute solution of an antimonious compound which has been rendered alkaline with sodium hydroxide and then strongly acidified with hydrofluoric acid, the antimony is *almost* completely precipitated as antimonious sulphide. If, however, either solution be mixed with large amounts of sodium acetate, the hydrogen sulphide precipitates the antimony as antimonious sulphide so completely that mere traces of the element remain dissolved. Some colorimetric determinations based on the observation that hydrogen sulphide produces in exceedingly dilute solutions of antimonious compounds a light yellow colour, the intensity of which is proportional to the amount of the metal present, indicate that the filtrate from the antimonious sulphide, precipitated from a hydrofluoric acid solution in which large amounts of sodium acetate have been dissolved, contains approximately four-tenths of a mgrm. of antimony per litre.

The determinations were made as follows:—

The fluorides in the filtrates from the antimonious sulphide were converted into sulphates by evaporation with concentrated sulphuric acid, and from a solution of the latter salts the traces of antimony were removed with hydrogen sulphide. The precipitates remained suspended in the solutions for days. Indeed, it was only after the lapse of about a week that they had settled so completely as to leave the supernatant liquids clear and limpid. They were light yellow in colour, and composed for the greater part of sulphur, which was extracted with alcohol and carbon bisulphide. In each case the unstained part of the filter-paper was cut away, and the remainder moistened with a few drops of concentrated hydrochloric acid; a small crystal of Rochelle salt was added; the solution warmed, diluted, and filtered into a Nessler cylinder. After introducing 10 cc. of water saturated with hydrogen sulphide and diluting to exactly 100 cc., the yellow colour was matched in the ordinary way. Five drops (0.25 cc.) of a N/100 solution of tartar emetic were always more than enough to produce in the standard of comparison a corresponding yellow tint.

Hydrogen sulphide produces no change in solutions of antimonious fluoride, either before or after the dissociation of the free acid has been repressed by the addition to the solution of a large amount of sodium acetate.

When a current of hydrogen sulphide is passed into (1) a moderately dilute solution of stannous fluoride containing free hydrofluoric acid, or into (2) a moderately dilute solution of a stannous compound which has been made alkaline with sodium hydroxide and then strongly acidified with hydrofluoric acid, stannous sulphide is precipitated. The precipitation of tin as stannous sulphide by hydrogen sulphide also takes place in either solution after it has been mixed with large amounts of sodium acetate. The precipitation seems to be only partial. (This may be due to the oxidising action of the air). Hydrogen sulphide produces no change when passed into a solution of stannic fluoride containing free hydrofluoric acid, either before or after the dissociation of the free acid has been repressed by the addition of large amounts of sodium acetate.

The behaviour of hydrofluoric acid solutions of arsenious and arsenic compounds toward hydrogen sulphide appears to be analogous to that observed in the case of similar solutions of the corresponding antimony compounds. There is, however, this difference:—The interaction of hydrogen sulphide and a solution of arsenic fluoride gives rise to the formation of sulphonyl-compounds, and ultimately a yellow precipitate, which is, in all probability, a mixture of arsenious sulphide, arsenic sulphide, and sulphur.

It goes without saying that the above reactions can be employed for detecting antimonious and antimonious,

stannous and stannic, and arsenious and arsenic compounds, respectively, where present together.

The fact that hydrogen sulphide precipitates from a hydrofluoric acid solution of antimonious and stannic compounds, after the dissociation of the free acid has been repressed by the addition of large amounts of sodium acetate, the antimony only, and that, too, practically completely, serves as a basis for an accurate and reliable quantitative method for separating these elements. (If we assume that Noyes's solutions contained both antimonious and antimonious fluorides we can see at once why his attempts to separate the element from tin were not more successful; the assumption is a reasonable one, for on merely treating antimony with concentrated nitric acid and evaporating to dryness we obtain, not antimonious acid, but a mixture of antimonious and antimonious oxides, or one composed of antimonious oxide and antimony tetroxide; A. Rose, *Pogg.*, 1841, liii., 161).

Since in the regular course of analysis antimony and tin are obtained in the form of sulphides, and since these sulphides are soluble in concentrated hydrochloric acid with the formation of antimonious and stannic chlorides, no difficulty is encountered in obtaining a solution containing the antimony in the lower, the tin in the higher state of oxidation. Moreover, sulphurous acid reduces antimonious to antimonious compounds, but has no action on stannic compounds.

The degree of completeness of the separation of the two elements by this method, involving the behaviour of hydrogen sulphide toward antimonious and stannic compounds in hydrofluoric acid solution, will be evident from the figures given below.

The preliminary measurements were made as follows:—At first known weights of re-crystallised tartar emetic were dissolved in measured volumes of carefully analysed stannic chloride solutions. To each solution, diluted somewhat and contained in a large platinum dish holding 500 cc., a drop of methyl-orange, sodium hydroxide to distinct alkaline reaction, and then 5 cc. of 48 per cent hydrofluoric acid were added. (The amount of hydrofluoric acid necessary will depend, of course, on the quantities of tin and antimony present; thus far 5 cc. have proved to be sufficient). After about half-an-hour, 10 grms. of sodium acetate were dissolved in the solution; it was diluted to 300 cc. and treated with a rapid current of hydrogen sulphide for one hour. (The colour of the solution changes from pink to yellow; the fluorides which sometimes separate out here dissolve immediately on diluting the solution). The rubber tubing from the gas generator was slung over the arm of a ring stand so that the paraffined delivery tube hung directly above the centre of the dish, and could be lifted or lowered until the end under the solution was about a centimetre above the bottom of the dish. By introducing the gas into the solution in this way there was no splashing, little sulphide adhered to the dish, and the delivery tube served as a convenient stirrer. The antimonious sulphide was filtered off *at once*, and washed with water containing acetic acid and saturated with hydrogen sulphide. (Water containing a little ammonium acetate and acetic acid seems to serve the purpose equally well). A glass funnel well paraffined was used, and the filtrate caught in cups made by cutting off the tops of old paraffin bottles which had contained hydrofluoric acid. Such cups are far superior to beakers coated with paraffin, for the paraffin coating in places frequently becomes loose and scales off. The filtrate was poured into the large platinum dish, 20 cc. of concentrated sulphuric acid were added, and the solution was evaporated on the water-bath. The dish was left on the bath until the residue was free from hydrofluoric acid. I found that a constant and thorough stirring with a platinum spatula of the thick syrupy residue served to promote the escape of the last traces of hydrofluoric acid. In no case was the residue heated until fumes of sulphuric anhydride escaped, for it was feared that by so doing traces of platinum would dissolve and subsequently interfere with the determination of the tin.

The residue in the dish was then dissolved in water, the solution poured into a large beaker, diluted to about 500 cc., and the tin precipitated with hydrogen sulphide as stannic sulphide. The latter was converted into the oxide by roasting, all the details given by Rose and Fresenius being carefully observed. Since the stannic sulphide, in spite of a thorough washing, is apt to retain a few tenths of a mgrm. of sodium sulphate, the resulting oxide was, after it had been ignited to constant weight in the presence of ammonium carbonate, extracted a number of times in the crucible with boiling water. After each addition of water the liquid was stirred, the oxide allowed to settle, and the clear liquid decanted through a very small filter-paper which was washed and burned, the ash being added to the contents of the crucible. A re-ignition of the oxide gave the weight from which the amount of tin was calculated.

	Tartar emetic.	Tin taken.	Tin found.	Tin.
	Grm.	Grm.	Grm.	Per cent.
1.	0.3047	0.1250	0.1242	99.36
2.	0.3326	0.1480	0.1481	100.06
3.	0.4679	0.1480	0.1476	99.73
4.	0.5100	0.1500	0.1498	99.87

(To be continued).

THE INSTRUMENTS AND METHODS OF RESEARCH.*

By L. A. BAUER.

WERE I to accuse you of forgetfulness, of shortness of memory, or possessed of that quality apt to prove troublesome to others, though characterised by the oldest of our past presidents, in his delightful "Reminiscences of an Astronomer," as a valuable quality—absent-mindedness—I daresay you would not be much offended, though possibly a trifle annoyed. But were I to accuse you of narrow-mindedness I might meet with a different reception. To none of us would it matter much to be called short-memory or absent-minded, but to be termed narrow-minded arouses our resentment immediately. But are we not all necessarily so, more or less, according to the circumstances in which we find ourselves?

Mind the Chief Instrument of Research.

I believe it was the mathematical physicist Stokes who said we must not forget that the chief instrument of investigation—the mind—is itself the object of research. To the Mind, then, we should devote our first and chief attention in the discussion of the subject set for this evening. How to reduce and check as far as possible this natural tendency of all of us to narrow-mindedness in one or more directions, or how, realising its necessary existence, to make due allowance for it in the formulation of conclusions which, though drawn with utmost care, are nevertheless subject to a "personal equation," is, as we at once readily see, a matter of the very highest importance.

Many of you are doubtless familiar with the Hindoo fable set to rhyme by Saxe:—

"It was six men of Indoostan
To learning much inclined,
Who went to see the Elephant
(Though all of them were blind),
That each by observation
Might satisfy his mind.

"The First approached the Elephant,
And happening to fall
Against his broad and sturdy side,
At once began to bawl:
'God bless me! but the Elephant
Is very like a wall!'

"The Second, feeling of the tusk,
Cried, 'Ho! what have we here
So very round and smooth and sharp?
To me 'tis mighty clear
This wonder of an Elephant
Is very like a spear!'

The third, happening to grasp the "squirming trunk within his hands," declared the elephant to be "very like a snake"; the fourth, feeling "about the knee," thought the elephant seemed "very like a tree"; the fifth, "chancing to touch the elephant's ear," described him as being "very like a fan," and when within the scope of the sixth came the swinging tail, the fact that the elephant "is very like a rope" was to him proved beyond dispute.

"And so these men of Indoostan
Disputed loud and long,
Each in his own opinion
Exceeding stiff and strong,
Though each was partly in the right,
And all were in the wrong!"

And now if you will permit me to slightly alter the poet's last verse, so as to point the moral to our own selves:—

"How oft in scientific wars
We disputants are seen
To rail in utter ignorance
Of what each other mean,
And prate about an Elephant
Not one of us has seen!"

What is Research?

In this day of encyclopædias numerous and ponderous, one is often struck with the fact that in spite of the manifest care and conscientious thought bestowed by the responsible editors, the omissions and evidences of discontinuity of treatment, and lack of recognition of the prime purposes of the compilation are as noteworthy as the imposing array of the results of our steadily advancing knowledge is startling. For a philosophic treatment—one fully appreciative of that which the student really requires, not only to enlighten him with regard to a particular subject, but also to stimulate him to research where it is most needed—I frequently get more satisfaction out of the older encyclopædias than from our modern ones, even though they can but present the status of the subject up to the time they were written.

As an illustration, take the word "research," appearing in our topic of this evening, or any of the associated terms—"discovery," "experiment," "investigation," and "observation." Turning to the index volumes of the ninth and tenth editions of the "Encyclopædia Britannica," I find but two references in which the word "research" appears—one to the exploring vessel, the "Research," and the other to "research degrees." Turning to the page on which the latter occurs, we find this interesting statement referring to Oxford University:—

"New degrees for the encouragement of research, the B.Lit. and B.Sc. (founded in 1895, and completed in 1900 by the institution of research doctorates), have attracted graduates from the universities of other countries. In 1899 a geographical department was opened, which is jointly supported by the University and by the Royal Geographical Society." Now comes the interesting statement which I beg to emphasise:—

"Of more bearing on practical life are the Day Training College Delegacy (1892) and the diploma in education (1896). Under the former elementary school teachers are enabled to take their training course at Oxford, and do so in growing numbers," &c.

We thus see what the writer of this article thinks of the relative value in practical life of research foundations and normal school foundations! Yet we all know that this view is not typical of that held in a country having such productive research organisations as the Royal Society or the Royal Institution. Sir Norman Lockyer in his luminous Inaugural Address before the British Association for the Advancement of Science, in 1903, on the "Influence of Brain-power on History," says:—"A country's research is as important in the long run as its battleships." Why, then,

* Address of the Retiring President, delivered before the Society, December 5, 1908. *Philosophical Society of Washington Bulletin*, vol. xv., p. 103.

does not the standard encyclopædia of that country make space for a representative article on "research."

Under "investigation" there also appears absolutely nothing. However, we have the "Investigator" ship, Investigator Shoal, Investigator Group, &c., but not a word about the general methods employed by "scientific investigators." And so it is with the word "discovery"—there is no reference whatsoever to an article on the general principles leading up to discoveries. Likewise with the word "observation." Though there are many references to observations of various kinds, there is no one article for setting forth the general principles of "observations" or the part they play in the discovery of fundamental facts. The same experience is had with regard to the word "experiment."

Now let us turn to an encyclopædia I invariably read with pleasure and profit; it frequently has supplied me with references to earlier work not to be obtained elsewhere. We shall find it instructive to us to-night, though the articles to which I beg to invite your kind attention were written three-fourths of a century ago. I refer to the classic Gehler's "Physikalisches Wörterbuch"—the revised edition by the noted investigators Brandes, Gmelin, Horner, Littrow, Muncke, and Pfaff, in 20 volumes, and published in Leipzig, 1825-1845. A veritable fund of information is found under the headings "Beobachtung" (observation) and "Versuch" (experiment). The article on "Beobachtung," by the physicist Muncke, embraces 28 octavo pages. He shows the distinction between "Beobachtungen" (observations) and "Versuche" (experiments) to be that the former pertain to the perceptions of phenomena presented to us by Nature in her unmodified course, whereas in the latter—in the experiments—we are seeking to produce certain results or phenomena, more or less looked for, in order either to verify a law already known or to disprove one suspected of being wrong or even to discover a new one. Both classes of experiences are necessary for a piece of investigation or research work.

Thus, we may behold either visually or in some other way certain striking solar phenomena; these belong to the class of observations which we ourselves are unable to modify in any manner whatsoever. Continued observation may, however, reveal a certain law which by experiment in the laboratory, conducted along more or less definite lines, we may seek to imitate in the hope of getting some clue to the *modus operandi* of the observed phenomena. In this article on "Observations" the author treats in detail the various elements entering into correct methods of investigation, condition of the observer and of his senses, his being unbiassed, character and errors of the instruments, errors of results, methods of increasing accuracy, representations of observations by graphs and formulæ, method of least squares, &c. He points out the mistake sometimes made, that an established formula satisfying the observed phenomenon within certain limits represents an actual law of Nature.

The article "Versuch" (experiment) consists of 44 pages, and is contributed by the astronomer Littrow. He shows that the most rapid development takes place in those sciences which afford the greatest opportunity for experimentation, referring, *e.g.*, to the slow and painful progress of the astronomer as long as he had to confine himself to mere celestial observations, and the comparatively rapid strides which occurred as soon as some of the observed phenomena could be either imitated by, or be compared with, those derived by laboratory experiment. The investigator, he says, must be absolutely free from preconceptions, and be careful, cautious, and unbiassed in his interpretation of what his senses may reveal to him. He illustrates how Man, called jokingly "das Ursachenthier" (the animal ever bent on ascertaining the cause of things), proceeds in ferreting out the why and wherefore of observed phenomena, and how his methods of circumspection develop with the advance of knowledge.

Though Man cannot determine the "Endursachen," or ultimate causes of things, the field open to him to discover

the laws governing phenomena or *vice versa*, classifying and enumerating those which follow a certain revealed law, is, nevertheless, still very large and sufficient to tax his energies. Witness, for example, the host of observed phenomena obeying the law of inverse squares!

The remaining sections of Littrow's article deal with the reduction of the experiments to the laws of motion, the numerical expression of the observed results in definite units, the importance of the part played by instruments or mechanical appliances, derivation of laws governing the observations, methods of ascertaining these laws, methods of reduction and of publication, and errors to be avoided.

These two articles will show sufficiently the character and scope of similar ones we should like to see in our standard English and American encyclopædias. ("Chambers' Encyclopædia" is found to contain a short article on "Experiments"; also one on "Observation"). Such information is contained in some measure at least, though not as comprehensively, in the modern German book of reference, Brockhaus's "Conversations-Lexikon," as also in the "Grande Encyclopædia" of the French. It is truly remarkable that there should be such an oversight in our "International Encyclopædia," when it is remembered that the editor-in-chief was one to whom research work owes a very great debt of gratitude indeed—the late and greatly lamented Daniel Coit Gilman. The only article found is one on "expert," and this pertains chiefly to "expert evidence" in courts of law. Yet what better statement concerning the "research or scientific spirit" could be made than contained in the following quotation from Gilman's writings?

"It is perpetually active. It is the search for the truth—questioning, doubting, verifying, sifting, testing, proving, that which has been handed down; observing, weighing, measuring, comparing the phenomena of Nature, open and recondite. In such researches, a degree of accuracy is nowadays reached which was impossible before the lens, the balance, and the metre, those marvellous instruments of precision, had attained their modern perfection. Wherever we look we may find indications of the scientific spirit. The search after origins, and the grounds of belief, the love of natural history, the establishment of laboratories, the perfection of scientific apparatus, the formation of scientific associations, and the employment of scientific methods in history, politics, economics, philology, psychology, are examples of the trend of intellectual activity. The readiness of the general government and of many State legislatures to encourage surveys and bureaus, the establishment of museums of natural history, and the support of explorations illustrate this tendency. Even theology feels the influence. The ancient and sacred proverb has been re-discovered—the letter killeth and the spirit maketh alive. I will go only to the edge of this disputed territory and shelter my own opinions behind those of a learned and devout prelate of the English Church (Bishop Walcott), whose words are these:—'No one can believe more firmly than I do that we are living in a time of revelation, and that the teachings of physical science are to be for us what Greek literature was in the twelfth century.' . . ."

"With the growth of the scientific spirit grows the love of truth, and with the love of truth in the abstract comes the love of accuracy in the concrete."—Extracts from the "Launching of a University," 1906, pp. 147-150.

Our foremost English dictionaries are, in general, not any more satisfying or edifying regarding the precise meaning of "research" in the scientific sense than are the standard encyclopædias. Their illustrations of the use of the word are usually neither apt nor sufficiently comprehensive.

How may we Sharpen Our Senses.

Of the senses, *sight* plays the greatest part in investigation. To this organ we have thus far devoted most attention to supplement and increase its natural powers by mechanical means—the telescope, microscope, &c. Next

would rank the sense of *hearing*; but the appliances for increasing our sensations in this respect are comparatively few, and still more is this the case with regard to the senses of *taste*, *smell*, and *touch*.

Yet what truly wonderful powers of touch are developed by the blind, and how extraordinary are the capabilities of certain animals for foretelling the distant approach of a deadly foe by the means of hearing or of smell!

Might not Man also, to his advantage, increase or stimulate his less-used senses in some manner, to the same degree, or approximately so, as that of sight? If he did, is it not possible that thereby he might have perceptions which would materially assist him in solving some of the vexed riddles of the universe? May he not for lack of proper development of these senses be in much the same plight as the "six blind men of Indoostan who went to see the elephant, though all of them were *blind*"?

If there is some possibility in this direction, how about the power of stimulating or interpreting our muscle sensations, the sensations of heat and cold, of pain, of pleasure, &c.?

Efforts have been made, as you know, to trace a definite connection between certain atmospheric phenomena and bodily sensations, or between the sensations to commit suicide or other crimes and certain meteorological conditions. Likewise are there attempts by well known men of science to sharpen and interpret the psychic sensations.

There is revealed here a field of research but little explored as yet—the increase of our powers of perception along other lines than chiefly those of sight. No one can foretell the future possibilities in these directions.

The doctrine of evolution teaches the result of long-discontinued use of any particular organ, and has familiarised us with the wonderful achievements of Nature brought about by sustained and continued effort along some definite direction. Both the physical and psychic condition of the observer requires their highest and healthiest development to insure not only the best results with the ever-increasing accuracy or precision required by the steady advance of knowledge, but also to bring about that round- or broad-mindedness needed for the proper interpretation of the results observed.

The Mathematical Instruments of Research.

A good-sized chapter might be written on the "Mathematical Instruments or Tools of Research." The predominating tendency of resolving or expressing every natural phenomenon—periodic or otherwise—by a Bessel or a Fourier series or by spherical harmonic functions has brought about at times, especially in geophysical and cosmical phenomena, if not direct misapplications, at least misinterpretations of the meaning and value of the coefficients derived.

Like a certain class of "naturalists," we also may have laid ourselves open to the opprobrious term of "Nature-Fakir," and instead of clarifying the situation our calculations may have actually contributed instead to "befog" it.

Frequently by the purely mathematical process there have been eliminated, in the attempt to represent a more or less irregularly occurring natural phenomenon by a smoothly flowing function, the very things of chief and permanent interest. The normal or average diurnal temperature curve, for example, or a uniform magnetic distribution over land, so as to yield perfectly regular lines of equal magnetic declination, never occur in Nature. There is thus being impressed upon us more and more forcibly the fact that what we have been regarding as "abnormal features"—the outstanding residuals between observations and the results derived from the mathematical formula—are in truth not "abnormal" from the standpoint of Nature, but are rather to be taken as indicative of the "abnormality" or "narrow-mindedness," which means the same thing, of ourselves in trying to dictate to Nature the artificial and regular channels she should pursue in her operations.

Louis Agassiz said:—

"The temptation to impose one's own ideas upon Nature,

to explain her mysteries by brilliant theories rather than by patient study of the facts as we find them, still leads us away."

The fundamental law of Nature is to invariably follow the paths of least resistance, and by examining these lines of structural weakness of the opposing systems we may have opened to us the very facts which are to be of real value and of sure benefit to mankind. The irregularity of the banks bordering a natural watercourse serves to differentiate the work of Nature from that of the builder of the artificial and regular channel.

No, instead of rejecting, we must learn to retain the outstanding residuals and study them most carefully and regard them as the true facts of Nature, and not those which we so egotistically and presumptuously try to force on her. What great discoveries may lie open to us when we once have grasped the true significance of the facts we have been so fond of measuring by our own standard and have been terming as "abnormal" or "irregular"!

An interesting example of not wholly successful applications of the continuous and ever-recurring functions of spherical harmonics to a typical geophysical phenomenon—the distribution of magnetism over the earth's surface—has been discussed by the speaker elsewhere. Though the number of unknowns has been increased in recent computations from the original 24 of Gauss to 48, nevertheless the difference between theory and observation is of such an order of magnitude as to preclude the use of the formula for even the purely practical demands of the navigator and surveyor. Nor has any one succeeded in giving any physical interpretation of the laboriously derived coefficients beyond the first three. And what do these three stand for? The simplest possible case of a first approximation to the actual state of the earth's magnetism, viz., that of a uniform magnetisation about a diameter inclined to the axis of rotation!

The prime difficulty here may be summed up in a word. The very surface over which the spherical harmonic functions are spread is itself such a prolific source of disturbance as to cause effects embracing a continent, a state, or a locality. Such a large number of terms would be requisite for an adequate representation as to make their computation prohibitive. We are dealing here with more or less discontinuous effects that cannot be imitated by continuous functions without leaving behind a train of residuals, precisely as though we were to try to fit to the actual configuration of the earth some standard pattern of our own. Let me ask what phenomenon have we, in fact, which will admit of the determination of 48, or even of 24, physical constants?

It had been my intention to say a few words on the value and limitation of that much-used as well as abused mathematical instrument of research, the method of least squares. Properly employed, it is a most useful adjunct to investigation; but, as intimated, the true significance of formulæ established by this method is at times pushed way beyond the limitations. What the tenour of my remarks might be will be sufficiently evident to you if I submit this query for your consideration: *What actual laws of Nature have been discovered by the method of least squares?*

The Mechanical Instruments of Research.

A few minutes were to have been given to the instruments employed by the scientific man to sharpen and amplify his natural senses and sensations—in a word, the tools furnished him by the mechanician. I am glad, however, both for your sake and mine, that this part of the subject was covered by an interesting paper presented at the previous meeting of the Society. It was emphasised there that for the best results it is essential that the investigator be able to work with instruments so constructed as to permit him to control or renew the various adjustments without the necessity of returning the instrument to the maker. The principle at times employed, which assumes that when adjustments are once made they are to "remain

put," is a very pernicious one. A number of very interesting examples from my own experience in the purchase and manufacture of magnetic instruments during the past ten years might be cited; but, as has been said, this part of the subject having already been covered, there is no need to dwell further upon it than to emphasise the injunction that the research worker, if he desires the best results, must know his instruments as thoroughly as himself.

Subjects of Research.

We come next to a brief consideration of the *subjects* of research, though not specifically mentioned in the title of our paper, yet implied in it. The rapid progress made by a science as soon as it reaches the stage of experimentation has already been noted. A crucial experiment has at times furnished information which by mere observation of phenomena, running their natural and unmodified course, might either have never come into our possession or at best would have taken a considerably longer time than that of the decisive experiment. You are all familiar with such cases, for almost every science can furnish examples.

Now it is an extremely interesting and suggestive fact that the greatest experimental discoveries to-day are not made in the older, well-recognised sciences, but on their borderlands—in the "twilight zone" of more or less related sciences. I have but to mention the words "physical chemistry," "physical geology," "astrophysics," "biochemistry," &c., and you will readily grant the assertion made. In the overlapping regions there seem to be the greatest opportunities afforded for solid, thorough, and at the same time remarkably rapid, experimental achievements. And so we are having produced almost daily new specialities or new sub-specialities.

What is the effect on the general broad-mindedness of Man by this extreme specialisation, so necessary for the production of the best and most far-reaching results? *Is the modern specialist more narrow-minded than the generalist of a century or two ago?* In view of our opening statements that the prime instrument of research is, after all, the mind, the question is, as you see, not an irrelevant one. We find statements occasionally made which would imply an affirmative answer to our question; but I, for one, would most emphatically protest against such an inference. I should maintain that the specialist, other things being equal, is likely to be a broader man than he who has no speciality, but simply a general knowledge of some particular science. The reason for my positive statement would be found in the fact mentioned, that the greatest part of the research work to-day is being done on the border-lands of the general sciences; for he who wishes to take part in this very active competition must needs be far better equipped than the mere generalist. The physical chemist, to be most successful, must have a very intimate knowledge of both physics and chemistry, and the more mathematical skill he possesses the better. The astrophysicist must be a physicist, a chemist, a mathematician, besides being an astronomer. And so with regard to the geophysicist.

Only a few names need be cited—like those, for example, of Faraday, Maxwell, Kelvin, von Helmholtz, Mascart—to support the contention that the bold physicists are, as a rule, those who have regarded their laboratory experiments and deductions therefrom merely as a means to an end, not an end in themselves, and who have accordingly sought to apply the knowledge gained to the solution of some of the great problems affecting the general welfare of Man. There is the greatest need in this country of well-trained and well-equipped physicists in the solution of the many perplexing problems of the earth's physics with regard to the phenomena of seismology, vulcanology, meteorology, atmospheric electricity, terrestrial magnetism, &c. When the investigator makes the attempt to apply some of his laboratory facts to geophysical and cosmical phenomena, he has opened to himself a world of which he never dreamed; he finds zest in familiarising himself with

the fundamental facts of other sciences in which until now he could take no interest.

Methods of Research; Discovery of Laws.

The methods in general have already received treatment in connection with the foregoing topics. It is always interesting to know what was the precise course followed in the discovery of a great law. However, no two investigators have ever pursued, or at least but rarely, precisely the same paths, and we must therefore be content with the statement of the general principles of research, such as has already been given.

A prevalent fault is observed in scientific publications whenever the investigator has had good training only on the observational side and but very little experience in scientific computing. He is very apt to violate one of the first and fundamental principles of good observing, viz., to employ such a method or scheme of observing as will yield but one definite result, and that with the highest possible accuracy and with the least amount of computation. Oftener than may be thought, schemes of observation are used which leave an arbitrary element to the computer, and in consequence a different result is forthcoming, according to who makes the computation. Had we time apt illustrations could readily be given from published works. The point made, that the observer must also bear in mind the computation side, and work up his results as soon as possible, is of fundamental importance in research work.

It may be worth while to consider briefly the insatiable desire of the analyst to ring in a series of sines and cosines to resemble the course of some natural phenomenon of which he does not know the exact law. Is this the old story over again, though in somewhat altered garb, of the epicycles and deferents of ancient astronomical mechanics, which received its highest development in the Ptolemaic System of the Universe? You will recall that Ptolemy, building on the suggestions of Apollonius and of Hipparchus, supposed a planet to describe an epicycle by a uniform revolution in a circle whose centre was carried uniformly in an eccentric round the earth. By suitable assumptions as to his variable factors, he was thus able to represent with considerable accuracy the apparent motions of the planets, and to reproduce quite satisfactorily other astronomical facts. This was the artifice employed by the astronomer of the period before the modern and more subtle art of simulating Nature, by the sine-cosine method, had become known.

What seemed so intricate and complex in Ptolemy's time could be expressed in very simple language indeed, when a Kepler discovered the true functions as embodied in his three fundamental laws. The present method of hiding our ignorance of the real law, which seems at times to exert such a mesmerising influence over us as to make us mistake the fictitious for the real, reminds one of the old conundrum: "Patch on, patch on, hole in the middle; if you guess this riddle, I'll give you a golden fiddle."

If the sine and cosine of the angle does not represent the curve of observation, patch on a sine and cosine of twice the angle; then, if necessary, thrice the angle; next, four times, and so *ad infinitum*! Now guess the riddle!

Of course I do not mean to discard this useful and in fact indispensable tool of research, but simply wish to call attention to its limitations and to the importance of not overlooking the fertile by-products, the residuals, which, because of our neglect of them, may some day rise and smite us in their wrath. Each one of us at one time or another has doubtless established, by least squares, an empirical formula of some kind which so beautifully fits the observations as to make us bold and venturesome. Now comes a new observation, somewhat outside of the range for which the expression was established. Eagerly the test is applied, and we find to our chagrin that the formula on which so much work had been spent will not fit the new result, and that we have a "counterfeit" and not a real law.

Let us suppose, for illustration, we are dealing with a phenomenon which almost entirely unfolds itself during the time between sunrise and sunset—the well-known diurnal variation of the earth's magnetism is a striking case of the kind. Following the usual method, the phenomenon is resolved into component parts with the aid of a Fourier series. The formula as generally adopted includes the four terms having, respectively, periodicities of twenty-four, twelve, eight, and six hours. For ordinary magnetic latitudes the striking result is obtained that the second term—the twelve hour one—is as important as the first or twenty-four one; so we might equally as well say “the semi-diurnal” as “the diurnal variation of the earth's magnetism.” In fact, as the semi-diurnal term unfolds itself twice in twenty-four hours, it is in reality more important than the purely diurnal one.

Does the resolution into Fourier terms of a phenomenon of the kind given really prove their existence in Nature? Can we conclude, without question, *e.g.*, that in addition to the diurnal term we also have a semi-diurnal one? Even with four terms, the series does not represent each hourly observation of the twenty-four with the same degree of precision. In fact, the residuals for the night hours are nearly of the same order of magnitude as the observed quantities. If the physical existence of the twelve-hour term is not proved, then there is no need of racking our brains as to its physical origin.

The difficulty disclosed by this example is of the same kind as the one treated in spherical harmonics, *viz.*, that we are attempting to represent a discontinuous function having a duration commensurate with that of the daylight hours by functions running smoothly through their individual courses for twenty-four hours.

Babbage, the inventor of the calculating machine named after him, said he once had the following question put to him:—“Pray, Mr. Babbage, if you put into the machine wrong figures, will the right answer come out?” Do we not at times attempt to put wrong premises into Nature's machinery and then expect correct answers?

We cannot close this section better than by quoting the following passage from the Address of the first President of the Society, Joseph Henry, given on November 24, 1877:—

“The general mental qualification necessary for scientific advancement is that which is usually denominated ‘common sense,’ though, added to this, imagination, induction, and trained logic, either of common language or of mathematics, are important adjuncts. Nor are the objects of scientific culture difficult of attainment. It has been truly said that the ‘seeds of great discoveries are constantly floating around us, but they only take root in minds well prepared to receive them.’”

Henry's insistence on the application in our scientific work of “common sense” reminds one of Clifford's apt definition of science as being “organised common sense.”

(To be continued)

NOTICES OF BOOKS.

Artificial Manures. By M. GEORGES VILLE. Translated and Edited by Sir WILLIAM CROOKES, D.Sc., F.R.S. New Edition. Revised by Sir WILLIAM CROOKES, D.Sc., F.R.S., and JOHN PERCIVAL, M.A. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1909.

In the new edition of this book, which is full of information of the greatest importance for the agriculturist both from the practical and theoretical points of view, the essential characteristics of the original have been preserved, and comparatively few alterations have been made in the text. The formulæ for the compounding of various manures have been adapted to modern requirements and to the needs of the English farmer. New matter dealing with recently adopted fertilising agents has also been added, and the

whole book has been subjected to a thorough revision. The author's vivid style of writing makes the book a very interesting one for the farmer who has but little knowledge of chemistry but who is not satisfied with following blindly the rule-of-thumb methods of his forefathers, while it is not too much to say that many of the general public and scientific men might find enlightenment in its perusal, especially if they regard agricultural problems as of vital importance, and recognise that upon the spread of a knowledge of agriculture and of interest in its operations intelligently performed the welfare of the human race to a large extent depends.

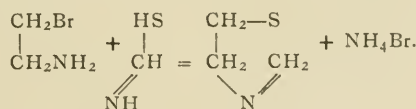
Merck's Reagenzien-Verzeichnis. (“Merck's Catalogue of Reagents”). Second Edition. Berlin: Julius Springer. 1908.

THE best methods of testing all kinds of reagents and drugs both microscopically and chemically are summarised in this work in a very concise form, and abundant references are given to the periodicals in which the tests were originally described. In most cases the experiments are described fully enough for the trained chemist to perform them without any further directions, but when they are exceedingly complicated, either as regards apparatus or method, no description is given, but only a reference to a journal or book where full directions can be found. The arrangement of the tests is alphabetical under the authors' names, the substances being indexed. For chemical and pharmaceutical laboratories the book is invaluable, and complete confidence may be placed in it, since the only tests given are those which have satisfied the requirements of a firm famous for the purity and reliability of its preparations.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xlii., No. 9, 1909.

Thioformamide.—Richard Willstätter and Theodor Wirth.—Thioformamide may be prepared by the action of phosphorus pentasulphide on formamide. Thus, an oily product is obtained, which exhibits the reactions of a thioamide. The isolation of pure thioformamide depends upon the fact that it yields a hydrate which is soluble in water, but unlike the oxygen compound is extracted from an aqueous solution by means of ether. Thioformamide crystallises in colourless prisms, which melt to a yellow oil at 28–29°. It decomposes readily. With one molecule of hydrochloric acid it forms a salt which is also very easily decomposed. The amide is tautomeric as shown by the formulæ $\text{H.C} \leq \text{SH}$, $\text{H.C} \leq \text{S}$, and it has an acid reaction on litmus. With chloroacetaldehyde it yields thiazol, and with bromethylamine the previously unknown thiazolin:—



When heated it decomposes chiefly into sulphuretted hydrogen and hydrocyanic acid, $\text{H.CS.NH}_2 \rightarrow \text{CNH} + \text{H}_2\text{S}$. Some of the hydrocyanic acid appears in the dimolecular form. The decomposition of the chlorhydrate yields sulphuretted hydrogen, hydrocyanic acid, ammonium chloride, carbon, carbon disulphide, and carbon monoxide.

Nitrosyl-Perchlorate.—K. A. Hofmann and Graf Armin Zedtwitz.—When anhydrous nitric acid is added to the hydrate of perchloric acid, $\text{ClO}_4\text{H} + \text{H}_2\text{O}$, colourless difficultly soluble crystals are formed. They can be prepared more easily by leading nitric anhydride into a solu-

tion of perchloric acid. Their formula is $\text{ClO}_4 \cdot \text{NO} + \text{H}_2\text{O}$. They are only very slightly hygroscopic, and deliquesce very gradually in moist air. An aqueous solution after warming gives both nitric acid and perchloric acid reactions. With amines nitrosyl perchlorate reacts very energetically, an explosion occurring if large quantities of substance are used. With phenols coloured products are obtained, and hence nitrosyl perchlorate can be used as a reagent for amines and phenols.

Sintering-point Curve.—Alfred Stock.—If the curve of the sintering-point (point at which drops of liquid appear) is plotted for mixtures of two substances, the composition of a compound can be detected far more clearly than from the melting-point curve. In the neighbourhood of the eutectics the curve becomes very nearly a straight line parallel to the axis, and where the compound is formed a very sharp maximum occurs. The sintering-point, *i.e.*, the point at which melting begins, is very easy to determine, and requires only a little material.

Existence of Phosphorus Disulphide, $\text{PS}_2(\text{P}_3\text{S}_6)$.—Alfred Stock.—The determination of the sintering-point curve of mixtures of P_4S_3 and P_2S_5 shows that a very marked maximum occurs, corresponding to the formation of a compound of formula P_4S_7 . This substance is also formed when a carbon disulphide solution of P_4S_3 and P_2S_5 is heated above 100° . The simplest equation expressing the reaction is $3\text{P}_4\text{S}_3 + 8\text{P}_2\text{S}_5 = 7\text{P}_4\text{S}_7$, but it hardly appears probable that this reaction occurs directly. There is no indication whatever of the formation of a disulphide, and P_3S_6 is in all probability non-existent. The substances previously taken for $\text{PS}_2(\text{P}_3\text{S}_6)$ are mixtures of P_4S_7 and P_2S_5 .

Displacement of Metals from Aqueous Solutions of their Salts by Hydrogen at High Temperature and Pressure.—Wl. Ipatiew and W. Werchowsky.—Using the metals silver, mercury, copper, zinc, cadmium, and lead the authors have studied the effects of hydrogen upon their salts at high temperatures and pressures, determining the amount of metal separated. They found that the influence of the temperature is very great; thus, at 70° and 129 atmospheric pressure a precipitate of cuprous oxide is obtained from copper acetate, while at 120° and 150 atmospheric pressure all the copper is separated as metal. The pressure is not without influence upon the result, although its effect is small compared with that of the temperature. Similar experiments with nickel, cobalt, lead, and bismuth showed that these metals are also separated from their salts by hydrogen at the corresponding temperatures and pressures. At lower temperatures basic salts are formed with cobalt, lead, and bismuth.

MISCELLANEOUS.

International Food Congress.—We have received the programme of the Second International Food Congress, to be held in Paris from October 17th to 24th (inclusive) next. So far as can be seen at the present moment, there are likely to be representatives present from every civilised country, and official delegates have been appointed by many governments. The particular object of the Congress is to define what operations are permissible in the handling of food and which follow upon the definitions which were accepted at the Congress held at Geneva last year. This programme is incomplete inasmuch as it does not contain the definitions and recommendations which will be put forward by the English-speaking world (the United States, the United Kingdom, the British Colonies, &c.). These, it is hoped, will form the subject of a supplementary programme which will be issued prior to the Congress. The interest which has been aroused in connection with this attempt to control the processes in use in connection with the manufacture of food products has been universal, and a very strong effort will be made to translate the findings of the Congress

into legislation in the various countries represented. The Congress will not only deal with ordinary food products, but will also discuss the methods of prevention of adulteration in chemical products, drugs, essential oils, spices, mineral waters, &c. The invitation to become delegates is extended to all who are in any way connected with the food supply:—Pharmaceutical associations, medical officers of health, sanitary officers, chemists, hygienists, provision manufacturers, cocoa, chocolate, and tea merchants, wine and spirit merchants, distillers, meat purveyors, ham and bacon curers, sausage makers, agricultural colleges, and generally all who in any way have anything to do with the preparation, distribution, or control of alimentary substances. The General Correspondent in the United Kingdom, Mr. Loudon M. Douglas, 3, Lauder Road, Edinburgh, will be glad to give any information which may be wanted in connection with the Congress, and will forward copies of the programme on receipt of a request to do so.

City and Guilds of London Institute.—At a meeting of the Council of the City and Guilds of London Institute held July 20th, it was resolved to award the diploma of "Associate of the City and Guilds of London Institute" to the following matriculated third year students of the Central Technical College who have completed a full course of instruction as prescribed by the Council:—*Civil and Mechanical Engineering.*—T. E. Beacham (Bramwell Medal), L. H. Swain, A. Mackinnon, J. L. Tann, B. A. R. Hughes, H. G. A. Clarke, L. B. Gilbert, E. Howe, T. A. Stephens, C. A. Shaw, F. R. Whitten, H. C. Thorpe, W. T. Thomas, A. B. B. Bevan, F. Grundy, M. Rodriguez, A. R. Sturgess, W. G. Quinton, G. Hepburn, H. P. B. Jones, W. L. Wright, J. L. E. Manes, L. A. Travers, L. E. Vyall, C. W. Jamieson, L. J. Coutanceau, N. M. Clougher, S. N. Chopra, S. E. Fitz-Simon, F. S. Vyall, H. M. Thompson, H. K. Korgaokar, G. M. Darwin, G. E. W. Hitchcock, H. T. M. Kent, L. del Cueto, C. T. B. Donkin, G. C. Wells, W. D. Bennett, J. Wadia, L. A. H. Winckler, J. W. Hunter, L. J. A. Vallet, W. Wise, A. Morant, C. G. Graham, G. W. Budden, A. R. Fraser, G. H. Harrington, R. O. Herford, G. B. Wickham, G. F. Hall, G. Osborn, T. R. S. Kynnersley, E. D. Pougnet, S. H. G. Osborne, G. L. Holzappel, C. G. Mitchell, G. C. Loughton, F. J. Cunningham, H. L. Burdett, C. M. Houfton, H. B. Harland, H. F. Cook, J. J. Castelain. *Electrical Engineering.*—F. H. Bramwell (Siemens Memorial Medal and Premium), A. Hutt, C. Higgins, H. Grinstead, R. A. Mack, A. Schmidt, C. G. Hawes, S. L. Smith, S. N. C. Whitehead, D. H. Hammonds, E. L. Reinert, F. P. Swann, W. C. McCallum, T. A. F. Dixon, J. Hollingworth, H. C. Hannam-Clark, L. G. S. Dodwell, C. D. Stoneham, R. W. Canning, H. G. Biggs, A. J. Anido, A. Weiss, B. A. Turkhud, W. B. Burford, J. O. Archer, J. R. A. Willey, E. H. Balcombe, J. H. P. Burchett. *Chemistry.*—E. H. Rodd, J. S. Arkinstall, R. T. Colgate, A. V. Campbell, F. W. Tilley. In addition to the above, certificates have been awarded to twenty matriculated third year students who have completed a full course of instruction at the Central Technical College, and to fifty-nine students who have completed a full course of instruction at the Technical College, Finsbury.

PRELIMINARY ANNOUNCEMENT.

A combined INDEX to the first 100 volumes of the CHEMICAL NEWS is now in course of preparation, and it is proposed to publish the same as soon as possible after the completion of the current (hundredth) volume. If any of our Readers have detected errors or omissions in any of the half yearly Indices, we should deem it a favour if they would draw our attention to the same before the end of this year.

THE CHEMICAL NEWS.

VOL C., No. 2593.

THE CONDENSATION OF RADIIUM EMANATION.

By A. LABORDE.

IN 1903 Rutherford and Soddy showed that radium emanation, when condensed at the temperature of liquid air in a copper tube, volatilises quite sharply when the temperature reaches about -150° .

M^{me}. Curie suggested that I should ascertain whether the nature of the wall of the tube in which the condensation is carried out has any influence upon the temperature at which the emanation escapes in the gaseous state.

I measured the temperature of volatilisation by a method similar to that of Rutherford and Soddy.

By means of a copper constantan thermo-electric couple I determined the temperature at which the emanation, condensed at -182.5° in a tube made of the material in question, is removed by a current of air which is free from water vapour and carbon dioxide.

(NOTE.—The couple was connected with a galvanometer of the Deprez-d'Arsonval type. It was standardised by taking as the points of adjustment the temperature of carbon dioxide in snow (-79.5°), that of the fusion of sulphuric ether (-117.6°), and that of liquid oxygen (-182.5°). At the low temperatures observed the deviation of the galvanometer produced a displacement of 1.5 mm. per degree on a scale placed 1 metre away. The tube was rolled into a coil, and embedded in granular copper in the interior of a Dewar's thermic insulator. Internal diameter of the tubes = 0.15 cm., length of the coils = 1.50 metres approximately. The velocity of the current of air was 0.26 cc. per second, corresponding to a linear velocity of the air in the coil of 15 cm. per second).

For this purpose I arranged at the end of the coil in the path of the current of air a little cylindrical condenser, in which the ionisation currents produced by the emanation could be measured by the quartz piezo-electric method.

I measured the temperature of volatilisation in copper, iron, tin, silver, glass, and silvered glass.

From my experiments it was found that radium emanation volatilises at the same temperature (-153° to -155°) in the four metals. But I observed that in glass volatilisation occurs at -177° to -179° , and in silvered glass at -175° to -177° ; i.e., $20-24^{\circ}$ lower than metals drawn out into tubes.

(NOTE.—I have proved that this lowering of the temperature of volatilisation in glass and in silvered glass is not due to the warming of the inner wall of the tube by the current of air; for this purpose the current of air was cooled in a metallic coil before it passed over the emanation condensed in glass).

These different experiments were performed, both with the metals and with glass, with quantities of emanation which varied from that produced by 0.0004 mgrm. of radium in equilibrium to that produced by 0.34 mgrm. of radium in equilibrium.

Moreover, I tried to find out how substances known to be good absorbents for certain gases would behave in similar experiments. I studied for this purpose cocoanut charcoal, which absorbs radium emanation very easily, as Rutherford has shown, meerschaum, platinum-black, and platinum sponge. (E. Henriot, *Le Radium*, Feb., 1908, has already studied this absorption at temperatures up to $+350^{\circ}$).

At the exit, also cooled, of a tin coil I arranged in the path of the current of air a little tube of thin glass of 4 mm. internal diameter, containing little fragments of the substance studied, spread over a length of 4 to 5 cm.

In these circumstances the results of the experiment were very different in the case of some substances. Thus, when the emanation was condensed in a metal, glass, or silvered glass tube it volatilised quite sharply; it caused in the mercury condenser placed at the exit from the cooled tubes an ionisation current, which increased very rapidly and passed through a maximum some minutes after the beginning of the disengagement. When, however, the substance placed in the path of the current of air was wood charcoal, meerschaum, or platinum-black, the disengagement of the emanation was much less sharp, and sometimes at the end of an hour the liberation of emanation had not ceased when the temperature had risen considerably. For small quantities of emanation the beginning of the disengagement might occur at a higher temperature than in the case of the metals.

These modifications in the experiment are not observed when platinum sponge is used.

The effect obtained with meerschaum and platinum-black may easily be explained if it is supposed that these two substances, like wood charcoal, are capable of absorbing radium emanation. Rutherford has already shown that a definite amount of emanation is absorbed by a given weight of charcoal at a given temperature. Thus it might be supposed that in my experiments the wood charcoal, meerschaum, and platinum-black, in proportion to the amount of heating, slowly give up the emanation which they have absorbed at lower temperatures.

From these different results it may be deduced that the nature of the wall has some effect upon the phenomenon of the condensation of radium emanation. It is not possible to affirm that absorption by the wall is the principal factor; however, when we remember that radium emanation is very easily retained by certain porous substances, such as wood charcoal, meerschaum, platinum-black, less easily and at a lower temperature by metals, at a still lower temperature by glass and silvered glass, the question arises whether all substances do not absorb radium emanation, but at different temperatures.

The temperature of absorption would depend rather upon the physical state of the substance than upon its atomic nature; thus, platinum-black seems able to absorb more emanation than platinum sponge, and silver drawn out into a tube retains it more readily than when deposited in a mirror.

It is possible that all substances like wood charcoal are capable of absorbing a limited amount of emanation at any temperature, this amount being very small in certain cases at high temperatures, as the experiments of P. Curie (*Journ. Chim. Phys.*, i., 409) on the absorption at the ordinary temperature show.—*Comptes Rendus*, cxlviii., 1591.

New Books.—Messrs. Williams and Norgate have just placed on the market here "The Chemistry and Literature of Beryllium," by C. L. Parsons, B.Sc., Professor of Inorganic Chemistry in the New Hampshire College. The book is written with the main object of saving preliminary study and labour to future investigators of beryllium, and to point out some of the peculiarities of this interesting element which are apt to lead the novice toward erroneous conclusions. The same firm are placing on the market immediately "Elementary Chemistry," by Frederic B. Emery, M.A. The method of presentation is the same as used by the author in his own classes, and nothing is included that has not been tried in both class-room and laboratory. It has been the aim of the author to make the text full yet condensed into a small size; this has been done by omitting repetitions and by the free use of cross references. Comparisons have been drawn in many cases, since the student learns more rapidly by comparison and contrast. Brief summaries are given at the end of each chapter, and illustrations have been freely used throughout. The work comprises nearly 700 pages, and is divided into three parts:—I. General Descriptive. II. Mathematical. III. Experimental.

THE
INSTRUMENTS AND METHODS OF RESEARCH.*

By L. A. BAUER.

(Concluded from p. 59).

Publication of Results of Research Work.

WE come next to the question of publication of the results of research. I think it may be taken as almost axiomatic that whatever is worthy of investigation should be made known in some effective manner, so as to reach without question those concerned. The multiplicity of literature on any one subject or even on any small portion thereof is now-a-days such that the worker finds it utterly impossible to keep abreast of publications, even those in his own field, to say nothing of kindred ones.

He is forced more and more to rely on abstracts—at least in so far as to direct him to that which he unquestionably must consult in the original, if possible. In my own particular line of work I rarely find that an abstract supplies all that is needed, and I almost invariably prefer to work directly with the original. I have heard similar statements from workers in other fields.

If it be true, then, that the investigator usually finds it necessary to consult the original publications, the next conclusion to be drawn is that the publication of any research work should, in general, be of such form and size as to permit the widest distribution possible, not only among the libraries and the principal seats of learning, but also among the workers and institutions immediately interested.

The scientific worker generally does not possess the means to purchase or to construct the instruments he requires for the prosecution of his work, and a book bearing in any way on the line of work to be pursued is as much to be considered part of his equipment as the purely mechanical tools. Indeed, I was told by the late von Bezold that Wilhelm Weber set his laboratory students to work by telling them, "Here are the instruments, and there are the *Annalen der Physik*; now go to work." The man of science usually wants his tools close by and within ready reach. He cannot afford to go to a distant library and then possibly find the book out. Private possession permits him, furthermore, to make marginal notes and references to enable him quickly to put his finger on the very thing needed.

Owing to these well-recognised needs, there has grown up a courteous and friendly interchange of publications among co-workers and sympathisers in the same field that to my mind deserves the highest encouragement. The time has unfortunately gone when scientific investigators can write such delightful and voluminous letters as passed between the research workers of half a century and more ago. The present system of interchange of publications has necessarily taken the place, to a very large extent, of the early letter writing. It is a system of gradual development along the lines of least resistance that it would be disadvantageous to contend against until some more effective means of intercommunication among scientific men has been devised.

But such free interchange of research publications can only be conducted to a limited extent, and can embrace only certain kinds of publications, viz., generally reprints or those of which the original cost for publication has already been borne in some manner, be it by a journal or by some research foundation. Larger publications, however, because of their expensiveness, must generally be restricted, for one reason or another, in their general circulation, with the inevitable result that the persons directly reached may be entirely out of proportion to the importance of the work undertaken.

Scientific men and scientific bodies could well afford to

pause and consider the tremendous cost of publication and the rather frequent waste of money incurred. Why is it, for example, that when an explorer gives an account of his travels in an unexplored region for the commercial press he finds it possible to say what he wishes in an attractive and handy octavo form, but when he is working for an endowed institution he feels compelled to present his matter in an expensive, ponderous, quarto form, inconvenient to handle?

It should be noted that it is as important to make research work known as to do it. To get our friends to read the contributions we may make to science requires now-a-days no little skill and diplomacy and an attractiveness of literary style on the part of the author not so essential in the days of less frequent printed works. The original purposes of important and costly expeditions are sometimes well nigh defeated or superseded, because of the delay in publication ensuing from the elaborateness of the plan adopted for the reduction of the field results and the form of publication decided upon.

Reduction in the pretentiousness, size, and cost of scientific publications appears to me to be one of the greatest needs of research to-day.

Methods of Research by Institutions.

Some time could profitably be spent on a consideration of the general agencies engaged in furthering research work and the methods employed for doing so. Being, however, connected with a "research institution," I should consider myself incompetent to enter upon a free and unbiassed discussion of the methods of such organisations for the furthering of research work. My remarks will be chiefly confined to a brief discussion of the methods to be used in certain investigations of a world-wide character. Craving your indulgence once more, I shall take as an example the general magnetic survey of the earth as representative of the kind of world-embracing research enterprises I have in mind.

Alexander von Humboldt, whose mental grasp was extraordinary in more than one science, set forth the following plan in his "Cosmos" for a general magnetic survey of the globe:—

"Four times in every century an expedition of three ships should be sent out to examine as nearly as possible at the same time the state of the magnetism of the earth, so far as it can be investigated in those parts which are covered by the ocean. . . . Land expeditions should be combined with these voyages. . . ."

"May the year 1850 be marked as the first normal epoch in which the materials for a magnetic chart shall be collected, and may permanent scientific institutions (academies) impose upon themselves the practice of reminding, every twenty-five or thirty years, governments favourable to the advance of navigation of the importance of an undertaking whose great cosmical importance depends on its long continued repetition. . . ."—The quotation is from E. C. Otté's translation of the "Cosmos," vol. ii., pp. 719—720.

Here was a noble project, universally conceded to be not only of the greatest scientific interest, but also of the greatest practical importance. Yet why is it that this grand plan has never been carried out by the foremost nations in friendly concert? Have our academies, as Humboldt suggested, never "imposed upon themselves the practice of reminding every twenty-five or thirty years governments favourable to the advance of navigation of the importance of an undertaking" of this character?

Instead of working along a common and definite plan, the magnetic operations hitherto have consisted of more or less isolated and incomplete surveys, independently undertaken by various nations and distributed over a great number of years. Not even for a single epoch has it been possible to construct the magnetic charts on the basis of

* Address of the Retiring President, delivered before the Society, December 5, 1908. *Philosophical Society of Washington Bulletin*, vol. xv., p. 103.

homogeneous material, distributed over the greater part of the earth, with some attempt, at least, at uniformity. And as to the possibility of constructing the charts, with the aid of similar data, for epochs twenty-five to thirty years apart, as Humboldt had dreamed, this, in spite of the enlightened interest of many countries, is even more remote.

Why should it have remained for a purely *research* organisation to undertake a problem touching so keenly as this on even the so-called sordid, purely practical interests of Man? Is it a fortunate fact that Humboldt's fascinating international scheme failed of execution, and that the chief brunt of the work is now being borne by a single organisation? It is not for the speaker to attempt to answer. The magnetic work of the Carnegie Institution of Washington has embraced, since 1904, a general magnetic survey of the Pacific Ocean, and land observations have been made in more or less unexplored regions in different parts of the world. The ocean magnetic work is to be undertaken next in the Atlantic Ocean, in 1909, on a specially built vessel, the first of its kind.

It is believed that an effective scheme of operation has been evolved, with the aid of the valuable advice received from eminent investigators. Without danger of giving offence to any one, it is possible to deal directly with the officials concerned, submitting to them our plans and ascertaining whether they contemplate doing anything similar, and, if so, whether, in case their funds are insufficient, they could suggest some friendly basis of co-operation between their organisation and ours. This plan of action has met with entire success thus far. Duplication, overlappings, and possible jealousies are all avoided; and in countries where no organisation whatever exists to do the work, we are free to go ahead and finish the task in less time than it would necessarily take to get an official action or official consensus of opinion from a large scientific body.

Slow deliberation in terrestrial magnetic work would be disastrous, for the prime reason that the phenomena of investigation in this field of research are continuously undergoing change. The time-element in the earth's magnetism, even for a period of a few years, is of such moment as to completely mask the fine hair-splitting points which would necessarily and rightly have to be raised on some international mode of action, to say nothing of the painful and cumbersome method which would have to be employed to conform with the rules of official correspondence between nations. Many a well and carefully executed magnetic survey in the past has had its full importance for world-wide investigation destroyed because of the possibility of error in the secular variation corrections which must be applied to bring its results up to the date of the later data.

Though I may be judged guilty of defending my own policy, I believe the course pursued by the Carnegie Institution of Washington in conducting the general magnetic survey of the globe is the only way in which this particular project, and similar ones to it, could not only be expeditiously conducted, but so as to realise the chief objects of the work. Judging from individual expressions received from scientific men everywhere, they appear in agreement with us. This policy, briefly stated, is: To make, with the aid of the friendly and harmonious co-operation of all concerned, a rapidly executed magnetic survey of the greater part of the globe, so that a general survey, all-sufficient for the solution of some of the great and world-wide problems of the earth's magnetism, will be completed within a period of ten to fifteen years. At a smaller number of points, selected in consideration of the prime questions at issue, the observations are to be repeated at intervals of five years or less, in order to supplement the rather sparsely distributed magnetic observatory data. Thus the determination of the corrections for reduction of the general work to any specific date is continuously provided for.

Now, had I the time or were this the place, I should like

to add a paragraph regarding the needful accuracy and the prime questions to be considered in the conduct of such a piece of work. Suffice it to say that the most evident result of all magnetic work in the past is that, for the purposes of a general survey, it is far better to make some sacrifice in accuracy if thereby it is made possible to secure observations at another point. In other words, the errors due to local disturbing conditions are far greater than the purely observational ones. Hence multiplicity of stations rather than extreme accuracy and laborious methods of observation and reduction is the prime requisite.

Stimulants to Research Work.

Dr. Gilman, in his charming reminiscences of the non-resident lecturers of the Johns Hopkins University, related the following of the great mathematician Sylvester:—

"Sylvester enjoyed stimulants—I do not mean such vulgar and material articles as alcohol and coffee. I never saw any indications that he cared for their support. But he loved such stimulants to intellectual activity as music and light, lively society, in which he was not called upon to participate. Once at a symphony concert I sat just behind him, admiring the dome of his capacious cranium, unconcealed by hair, and I noticed how absorbed he was. The next day, Sunday, he came to me impetuously to say that he had worked out some mathematical proposition at the concert of the evening before, the music having quickened his mathematical mind. He really thought this was his greatest achievement yet, and he had hastened to write it out and mail it to the Academy of Sciences in Paris. Once he told me that, having a special paper to prepare, he went to a store and bought a pound of candles, which he placed about his room, on all sorts of extemporaneous candlesticks; 'for light,' he said, 'is a most powerful tonic.'"

These anecdotes will serve to recall similar ones of noted men, and many of you, doubtless, were this an experience meeting, could easily occupy the balance of the evening in delightful recollections of what each has found best to stimulate him to renewed intellectual activity, and I dare say that many of you would unite with me in declaring that membership in this Society has been one of the most helpful and stimulating influences.

We really have much to be proud of in the history and membership of the Philosophical Society of Washington. I should indeed consider myself remiss in the duties imposed upon me by the subject selected did I not refer at least to the eminent part this Society, through its members, has taken in bringing about the wonderful appreciation of scientific work and scientific methods we are to-day witnessing in our country. There have been several notable addresses by past presidents that might advantageously have been reviewed in connection with our topic. But we lack the time.

I cannot refrain, however, from quoting once more from Henry's address, already referred to, which I hope you may be induced to read in its entirety:—

"Man is a sympathetic being, and no incentive to mental exertion is more powerful than that which springs from a desire for the approbation of his fellow men; besides this, frequent interchange of ideas and appreciative encouragement are almost essential to the successful prosecution of labours requiring profound thought and continued mental exertion." * * *

"It is an essential feature of a scientific society that every communication presented to it should be subject to free critical discussion. Such discussion not only enlivens the proceedings, but is generally instructive, frequently eliciting facts which, though insignificant when isolated, when brought together mutually illustrate each other and lead ultimately to important conclusions."

Conclusion.

My address began with statements revealing the necessity of keeping our minds ever open and free for the careful weighing and the unbiassed reception of the facts observed

and discovered. Throughout I have attempted to lay chief stress upon the mental and human elements involved in the topic. I cannot do better in closing than to quote you a sentence from a letter ("Life and Letters of Herbert Spencer," by David Duncan, vol. ii., p. 163) which the great mathematical physicist, James Clarke Maxwell, wrote to Herbert Spencer on a subject of controversy in the latter's "First Principles," viz.:—

"It is very seldom that any man who tries to form a system can prevent his system from forming around him, and closing him in before he is forty. Hence the wisdom of putting in some ingredient to check crystallisation and keep the system in a colloidal condition."

Let our watchword therefore be: *ever to keep our systems—our theories—in a colloidal condition!*

PREPARATION OF PURE CERIUM SALTS AND THE COLOUR OF CERIUM OXIDE.*

By ARTHUR C. NEISH.

THE close relationship of the analytical behaviour of the elements in the cerium group offers great difficulty in separating pure cerium salts. The lack of delicate tests for the elements, other than cerium, makes the preparation of any reagent, so that at present the spark spectrum is not only a sure test for purity. The colour of pure cerium oxide, CeO_2 , has been much disputed, since many of the supposed pure cerium preparations were not pure; the different colours given this oxide, as found in the literature, offers a suggestion for research as well as the preparation of pure cerium salts.

From a review of the different methods proposed for the preparation of pure cerium salts, it was decided to make the process of purification in steps, using the best method for the elimination of each element usually found in the starting material, and repeating these to insure complete purification. Methods involving lengthy crystallisations were omitted. The starting material was the crude oxalate obtained from the Welsbach Company, and it was assumed to contain as impurities all the rare earths found in monazite sands, together with iron, aluminium, calcium, and magnesium. Didymium and iron were easily recognised impurities, the absorption bands were very marked.

The method finally adopted consisted of six distinct steps:—

1. *Hydrochloric Acid Treatment* to remove iron, calcium, &c.—The crude oxalate (150 grms., 50 grms. in each of three beakers) was warmed for an hour on the water-bath with 750 cc. of 1 per cent hydrochloric acid, and washed by decantation and on a Büchner funnel with 1 per cent hydrochloric acid and hot water. This was repeated successively with 350 cc. of 0.5 per cent and 350 cc. of 0.2 per cent hydrochloric acid, and washed as before until the colour test for iron, with solid ammonium thiocyanate and amyl alcohol, was no greater than that for a blank test.

2. *Ammonium Oxalate Treatment* to remove thorium, zirconium, and yttrium.—The oxalate from the above treatment was removed from the funnel, a third placed in each beaker, and a hot solution of ammonium oxalate, saturated in the cold, was added. The beakers were heated on the water-bath with frequent stirring for an hour, and allowed to settle. The oxalate settled rapidly, and changed from a fine powder to a distinct crystalline condition; it was filtered through a Büchner funnel, washed with 500 cc. of ammonium oxalate solution, and well with cold water. This treatment was repeated three times, and, on account of the tendency for the oxalate to form lumps, it was found advisable to grind it up in a mortar with ammonium

oxalate solution to a thick cream before transferring it to the beakers for the successive treatments.

3. *Potassium Hydroxide Treatment* to remove aluminium, &c.—The oxalate was transferred to a mortar, made into a cream with water, and transferred one-third to each beaker; 75 grms. of stick potassium hydroxide (purified by alcohol) were added to each beaker, and water added to about 500 cc. They were then heated with constant stirring to boiling, then on the water-bath for half an hour, diluted to the capacity of the beaker, allowed to settle, filtered through a Büchner funnel, and well washed with about three litres of hot water. The oxalate soon changed to hydroxide; the change was marked by the flocculent appearance of the precipitate as compared with the crystalline and heavy nature of the oxalate; the colour changed from pure white to a greyish white, but on dilution with much water the colour changed to drab, and when placed in the funnel, especially when the potassium hydroxide was removed and the washing commenced, the surface turned a deeper drab and gradually turned so throughout the mass. On longer exposure to the air the surface turned purple, then reddish brown, and finally canary-yellow; the yellow was undoubtedly due to a ceric condition, and the other colours to intermediate stages of oxidation.

4. *Sulphuric Acid and Potassium Sulphate Treatment* to remove yttrium, ytterbium, erbium, and samarium.—Many experiments were tried on a small scale as to whether dilute or strong acid effected solution best. The stronger acid was considered to be the more effective, but in both dilute and strong acid the precipitate could not be all dissolved by boiling, as cerous sulphate was more insoluble in the hot than in the cold. Jolin states that 100 parts of water at 0° dissolve 16 parts of anhydrous sulphate, while at 100° only 2 parts dissolve. The supernatant liquid had an opalescent appearance suggesting a basic salt; the addition of 10 to 20 cc. of hydrogen peroxide to each beaker of solution caused the solution to clear up on boiling, and more sulphate went into solution. About one-third of the hydroxide was transferred to each beaker, 300 cc. of water added, 30 cc. of 50 per cent sulphuric acid added at intervals, and heated to boiling. The peculiar colour of the hydroxide soon disappeared and instead a white crystalline salt was deposited. A little more acid was added and boiled, a little hydrogen peroxide (10 to 20 cc.) added, again boiled until all peroxide was decomposed, allowed to stand, and the clear supernatant liquid was poured off. The complete removal of the peroxide was determined by making some of the solution ammoniacal, and if any peroxide remained a yellow colour or precipitate appeared; a white precipitate indicated complete removal. The volume in each beaker was then made up to about 600 cc., cooled to about 10° in order to dissolve as much as possible, the supernatant liquid poured off, more water and a little acid added, boiled, a little hydrogen peroxide added, boiled, cooled, and treated in this manner until all went into solution. In all the volume was about three litres, and about 90 cc. of 50 per cent sulphuric acid were used. During solution a brisk evolution of gas was noticed. This was carbon dioxide and oxygen from the decomposition of the carbonate and ceric salt.

This solution was placed in a large evaporating dish, and 100 grms. of potassium sulphate dissolved in 500 cc. of boiling water added; crystals deposited immediately. It was allowed to stand over night, heated, and 50 grms. more of potassium sulphate, as solution, added and allowed to cool. If no more crystals form enough has been added. It was thought to be advantageous to heat after the addition of potassium sulphate, the potassium sulphate being more soluble, the cerous sulphate less soluble, so that the formation of the double salt was a slow one and the crystals attained a larger size. When the cool supernatant liquid was poured off, the crystals were washed with warm water to dissolve out the excess of potassium salt. Some of the double sulphate was ignited and gave an oxide with a pink tint.

5. *Potassium Hydroxide and Chlorine* to remove

* Read at the Toronto Meeting of the American Chemical Society, June, 1907. From the *Journal of the American Chemical Society*, xxi., No. 5.

lanthanum and didymium.—The crystals of double sulphate were transferred to the three beakers, water added to about three-quarters full, 20 cc. of concentrated hydrochloric acid added, digested on the water-bath for half an hour, and the supernatant liquid poured into an evaporating dish. This was continued until all went into solution; a total of 250 cc. of concentrated hydrochloric acid were used. To this solution stick potassium hydroxide was added in excess, and heated until all the cerium was precipitated as hydroxide, and the filtrate gave no test for cerium after acidifying and adding hydrogen peroxide and ammonia. It was then filtered through a Büchner funnel and well washed with hot water to remove the excess of alkali and potassium salts. The precipitate of hydroxide was transferred to a tall cylinder, capacity about 2300 cc., water added to about 2100 cc., and then 200 grms. of potassium hydroxide. An electric stirring apparatus was used to keep the hydroxide well mixed, a stream of chlorine added very slowly, a bubble at a time, until completely saturated (twenty hours), and allowed to settle. The supernatant liquid was syphoned off, water added, and stirred for fifteen minutes, allowed to settle, syphoned, and repeated twice, making three washings with water. The colour of the ignited oxide from this treatment was a little improvement over the oxide made from the original sample, showing the presence of a considerable amount of didymium. It was thought that a stronger potassium hydroxide solution would be better; to accomplish this the precipitate, yellow hydrated ceric oxide, was transferred to a Büchner funnel and washed with hot water. The precipitate was transferred to a large evaporating dish, treated with 1500 cc. of water and 150 to 200 cc. of concentrated hydrochloric acid. The yellow peroxide did not dissolve completely in the acid, but on the addition of a little hydrogen peroxide it quickly dissolved to a clear colourless cerous solution. The cerous chloride was treated with potassium hydroxide as before, boiled, filtered, and washed on the funnel. The moist hydroxide was transferred to the cylinder, 1000 grms. of potassium hydroxide added, and the volume made up to about a litre and a-half, chlorine run in until completely saturated, allowed to settle, and the supernatant liquid syphoned off. A litre of potassium hypochlorite solution (20 per cent KOH) was added, stirred for five hours, and the clear liquid syphoned off. The cylinder was again filled with water, 25 grms. of potassium hydroxide added, and chlorine run in to saturation, allowed to settle, and the clear liquid syphoned off, filled with water, stirred, filtered, and well washed with water. The yellow precipitate was treated as before with water and hydrochloric acid, the solution was cleared and reduced with hydrogen peroxide, and the cerium precipitated as hydroxide, filtered, washed, and transferred to the cylinder. About 2000 cc. of water were added, and 1000 grms. of potassium hydroxide, chlorine run in quickly at first and slowly to complete saturation. The precipitate was allowed to settle, the supernatant liquid syphoned off, water added, stirred, and this run off; the whole was transferred to the funnel, and well washed with water to remove potassium salts.

6. *Hydrochloric Acid and Oxalic Acid* to remove iron, &c.—The yellow precipitate was transferred to a large evaporating dish, about 1500 cc. of water and 150 cc. of concentrated hydrochloric acid added, and boiled. After most of the precipitate had dissolved, hydrogen peroxide was added to take all into solution and reduce the ceric to the cerous condition. To the cerous chloride solution 500 cc. of concentrated hydrochloric acid were added, and heated almost to boiling; then 1000 cc. of oxalic acid solution (saturated in the cold) added; this gave no precipitate while hot, but on cooling crystalline oxalate of cerium separated; this was called "first crop." The first crop of crystals was filtered through a Büchner funnel and well washed with hot water, and dried between filter-papers in the air. This cerium oxalate was considered pure. To the mother-liquor 1000 cc. of oxalic acid solution were added and allowed to crystallise, about the same

yield was obtained; this was filtered, well washed and dried in the air, and called "second crop." The oxide obtained on ignition from "first crop" was free from a red tinge due to iron and didymium, but had a yellow tint the colour of chamois leather. The oxide from "second crop" had the same colour.

When some of the oxalate, first crop, was heated in an atmosphere of pure dry hydrogen it charred brown, and became black on continued heating, and stayed so when cooled in an atmosphere of hydrogen. When this black compound was heated in an atmosphere of pure oxygen a glow ran over the powder, and a precipitate was produced by leading the products into lime-water. The powder turned a canary-yellow, and on higher heating to an orange, on cooling in an atmosphere of oxygen it assumed a light yellow, the colour of chamois leather. Another sample of first crop was heated in air free from carbon dioxide and moisture, the oxalate changed to a canary-yellow oxide, a narrow black band preceded the change to yellow; and in the deeper parts it glowed. When these two oxides were heated in hydrogen they turned a dirty green, a little the colour of graphite, and on cooling them in hydrogen both turned a yellow-brown. On heating both in pure oxygen they turned pale yellow, deeper in colour at higher temperatures, and when cooled in air they turned light yellow, the same colour as mentioned above.

This work was carried out in the autumn of 1903, but on account of the inability to have a spark spectrum analysis made it was abandoned. Through the kindness of Prof. J. S. Ames and Mr. Frank L. Cooper, of Johns Hopkins University, a careful analysis of the two crops was made with the following results:—

"Sample A (first crop) contains a trace of lanthanum and the merest trace of yttrium." "The same is true of sample B (second crop)." From this one was justified in calling the products pure; the trace of lanthanum indicated that more thorough treatment with chlorine was necessary, the precipitate should have been more thoroughly washed, dissolved, and re-precipitated each time before the addition of the alkali and chlorine. The presence of the trace of yttrium was undoubtedly due to the separation by the double sulphate, although yttrium is soluble as well as thorium in ammonium oxalate. The cause of contamination with yttrium was not due to lack of resolution and re-precipitation, although this would have undoubtedly improved it, but to the error in heating the sulphate solution after the addition of potassium sulphate, causing the yttrium sulphate and cerium sulphate, which are more insoluble in the hot than the cold, to separate out, or perhaps to hydrolysis, a property very marked in the cerium earths.

With the following additional operations the method gives a pure product. In 4, the sulphuric acid and potassium sulphate treatment, do not heat the solution after the potassium sulphate has been added but add it to the cold solution. Dissolve this double sulphate with potassium hydroxide and re-precipitate the double sulphate. This should remove this mere trace of yttrium.

In 5, the treatment with potassium hydroxide and chlorine, more thorough washing by decantation and on the filter was needed; the precipitate of peroxide should have been dissolved in acid, &c., after each oxidation with chlorine, re-precipitated with alkali and chlorine added, instead of adding fresh alkali to the peroxide and adding chlorine. This modification should remove the traces of lanthanum.

The finished product showed such marked purity that a spectrum analysis of the starting material was to have been made by Prof. Ames, but due to the carelessness of an express company the only sample was lost. I was unable to get more of the same lot from the Welsbach Company, although they said the crude oxalate was of constant composition. A sample from another lot, about the same date of manufacture, was obtained, and this as well as the original sample revealed the presence of didymium in considerable quantities by the absorption spectrum. A sample of the new crude oxalate was sent to

Prof. Ames and Dr. Cooper, and after an unavoidable delay Dr. Cooper reports:—"The crude oxalate was very impure and contained a large amount of neodymium, praseodymium, lanthanum, yttrium, thorium, besides calcium, &c., also tantalum." Columbites and tantalites are often found in monazite sands, accounting for the presence of the last named impurity.

Summary.

The method herein stated, with the slight additional precautions mentioned, offers a good method for preparing pure cerium salts from crude oxalate. In case the starting material was a sand or mineral, the method for solution and precipitation of the rare earths as oxalates, see *Journ. Am. Chem. Soc.*, 1904, xxvi., 780.

The colour of ceric oxide is a pale chamois colour; colours of a reddish or pink indicate the presence of coloured oxides; a very pale or almost white oxide indicates the presence of white oxides as impurities.

The colour of pure ceric oxide is not due to the presence of nitrogen from the air, since the colour is the same if ignited in pure oxygen.

The author wishes to thank Mr. H. S. Miner, and Mr. M. C. Whitaker, of the Welsbach Company, for samples of material and advice, and especially to thank Prof. Ames and Dr. Frank L. Cooper for the time spent and interest taken in establishing the purity of the products and the impurity of the starting material.

The purity of the finished product is further established by the work of Metzger in this issue; the sample is named by him "4."

THE SEPARATION OF TIN AND ANTIMONY.*

By LEROY W. McCAY.

(Concluded from p. 55).

I NEXT determined electrolytically, according to the directions given by Classen, the amount of antimony present in the sample of re-crystallised tartar emetic. (Potassium cyanide instead of sodium sulphite was used to do away with the disturbing influence of the polysulphides).

	Tartar emetic. Grm.	Antimony found. Grm.
1.	0.5100	0.1912
2.	0.5100	0.1911

These figures are markedly higher than theory demands. (Expressed in percentages they agree quite well with the results of Classen, who used tartar emetic as a standard substance in testing his electrolytic method for determining antimony; see Classen, "Quant. Analyse durch Electrolyse," 1879, p. 193). However, as will be seen below, they agreed very well with those found on determining in the same way the antimony in the antimonious sulphide obtained in the separation of the element from tin.

	Tartar emetic. Grm.	Tin taken. Grm.	Antimony found Grm.	Tin found. Grm.
1.	0.5100	0.1500	0.1905	0.1501
2.	0.5100	0.1500	0.1912	0.1497

The coatings of antimony dissolved completely in concentrated nitric acid containing some Rochelle salt. They were free from tin, for when 0.2 gm. of pure antimony, to which a little granule of tin, weighing about a mgrm., had been added, was treated with concentrated nitric acid containing some Rochelle salt, a small residue of stannic oxide remained. I could not detect antimony with certainty in the oxide of tin. It was, in each case, converted into the sulphide by fusing it with sulphur and sodium carbonate, dissolving the sulpho-salt in water, and acidifying the solution with sulphuric acid. The well washed sulphide was then dissolved in concentrated hydrochloric acid, the solution warmed and filtered into a small platinum dish, where

it was permitted to act on a roll of pure iron wire, at a gentle heat, for several hours. At the end of this period the dish was still bright, the solution being of a light green colour. To convince myself of the delicacy and reliability of the test I now added to the solution three drops of a N/100 solution of tartar emetic. In less than ten minutes the surface of the dish was covered with a distinct brown stain.

Since it is well known that the electrolytic method for determining antimony yield results which are generally high, I do not insist on the accuracy of the above figures. However, as I have already intimated, they do show that the separation of antimony and tin according to the course of procedure under discussion is practically complete. That the results for the tin are satisfactory is evident at a glance.

It seemed best at this point to discard the tartar emetic and start out with pure metallic antimony, also to determine the antimony by another method.

A standard solution of antimony was prepared by dissolving about 5 grms. of the purest antimony I could obtain in concentrated hydrochloric acid with the addition of potassium chlorate, heating the solution on the water-bath until all free chlorine was expelled, adding a considerable amount of tartaric acid, and diluting to 1 litre. The antimony in 25 cc. of this solution was then carefully determined according to the directions given by Fresenius, with the exception that the mixture of antimonious and antimonious sulphides and sulphur was collected in a Gooch crucible over asbestos, and heated at about 300° to blackness in a Henz furnace (*Zeit. Anorg. Chem.*, xxxvii., 10), and in a current of carbon dioxide. Three determinations were made.

	Found (grm.).
1	0.1225
2	0.1228
3	0.1224

Average 0.1226 Sb.
25 cc. = 0.1226 gm., 20 cc. = 0.0981 gm.

I also prepared for this series of separations a new tin solution by dissolving exactly 6 grms. of Kahlbaum's purest tin in concentrated hydrochloric acid with addition of potassium chlorate. After getting rid of all the free chlorine by warming the solution on the water-bath, 20 grms. of tartaric acid dissolved in a little water were added, and the solution was diluted to a litre. Here, too, the tin was determined in 25 cc. It was precipitated from a volume of about 600 cc. with hydrogen sulphide as stannic sulphide, which, after a thorough washing with water containing ammonium acetate and acetic acid and drying, was converted into the oxide by roasting.

Found, 25 cc. = 0.1502 gm. Sn.

This figure agrees well with the calculated amount, 0.1500 gm.

The separations were made as follows:—20 cc. of the antimony and 25 cc. of the tin solution were pipetted into a beaker holding about a litre, the mixture was diluted to 600 cc., and the metals were precipitated as sulphides with hydrogen sulphide. In each case the gas was passed for one hour. After standing over night in a warm place the dark brown precipitate was filtered off and washed with water containing ammonium acetate and a little acetic acid. In the first two cases (separations 1 and 2) each precipitate was dried at 70–75°, as much of it as possible transferred to a clock glass, and what remained adhering to the filter-paper dissolved in a few drops of yellow ammonium sulphide, the solution and washings being caught in a small beaker. After evaporating this solution to dryness on the water-bath, the main portion of the precipitate was brushed into the beaker, the latter covered with a watch-glass, the precipitate moistened with a few drops of water and treated with 5 cc. of concentrated hydrochloric acid. The beaker was placed on the simmering water-bath, and allowed to remain there until all the

* From *Journal of the American Chemical Society*, xxxi., No. 3.

hydrogen sulphide had been expelled. The solution was then diluted with a little water containing tartaric acid, filtered into the large platinum dish, neutralised with pure caustic soda, and acidified with 5 cc. of 48 per cent hydrofluoric acid. To repress the dissociation of the hydrofluoric acid, the same amount of sodium acetate was used as was employed in the former separations. The solution was now diluted to 300 cc. and the antimony precipitated with hydrogen sulphide as already described. Since the results for the tin were a trifle low, and an examination of the residues of sulphur proved that the extractions were not complete, the mixture of the sulphides in each of the next experiments (separations 3 and 4) was not dried, but after as much water as possible had been removed with the filter-pump, treated at once with concentrated hydrochloric acid. This was accomplished by cutting away the unstained half of the filter-paper and submitting the other half carrying the precipitate to the action of the acid. A beaker of 100 cc. capacity was employed. It was covered with a watch-glass and gently heated on the water-bath until the hydrogen sulphide was expelled. During the digestion on the bath the paper was kneaded to a fine pulp with a glass rod. When the last traces of hydrogen sulphide had disappeared, 2 grms. of tartaric acid dissolved in 5 cc. of water were added, the solution was diluted to about 20 cc. and filtered into the platinum dish. Since even in these circumstances the paper pulp was found to retain traces of antimony and tin, it was dried, extracted with carbon bisulphide, and again treated with concentrated hydrochloric acid. In this case, however, only about 1 cc. of the acid was used. If very accurate results are required, this second treatment with the acid should not be omitted. Whether the sulphur forms a protecting coating about some of the sulphides, or whether small amounts of difficultly soluble sulphochlorides are formed during the action of the hydrochloric acid, is a matter which has not yet been cleared up.

The antimonious sulphide was collected in a large platinum Gooch crucible over a disc of hardened filter-paper, the filtrate being caught in a paraffin cup, placed under a bell-jar resting on a ground glass plate, and provided with the necessary adjustments for filtering by suction. To avoid splashing the cup was covered with a paraffined clock glass with a hole in the centre through which the lower end of the paraffined crucible support was passed. After washing the precipitate with water containing ammonium acetate and acetic acid, then with water, and finally with alcohol, it was dried to constant weight at 110°. The weight of the crucible and disc, also dried at 110°, having been previously determined, the weight of the amorphous red sulphide was obtained. The greater part of it was then heated to blackness in a little porcelain boat in a current of carbon dioxide gas, according to the directions given by Fresenius. The weight of the crucible and disc along with the rest of the precipitate was determined, and from the various data the amount of antimony calculated.

This method for filtering off the sulphide and determining the antimony works admirably, and leaves little to be desired. That the antimony in the red precipitate can be determined at once by dissolving the latter in concentrated hydrochloric acid alone, or in concentrated hydrochloric acid with the addition of potassium chlorate, and making use of the volumetric methods of Mohr or Weller, will be evident to all analysts.

The tin in the filtrate was determined according to the process outlined above. Owing to the charring action of the sulphuric acid on the tartaric acid the solution of the tin is of a marked brown colour, but no difficulty has been experienced in effecting a complete precipitation of the metal with hydrogen sulphide. The stannic sulphide appears to act as a mordant, for in settling it extracts the brown colouring matter from the solution, leaving the supernatant liquid, when subsidence is complete, perfectly colourless.

The last two separations are most satisfactory, and

prove that the second method for dissolving the mixture of the sulphides is to be preferred.

	Sb taken.	Sb found.	Sn taken.	Sn found.
	Grm.	Grm.	Grm.	Grm.
1.	0.0981	0.0987	0.1500	0.1491
2.	0.0981	0.0986	0.1500	0.1490
3.	0.0981	0.0981	0.1500	0.1502
4.	0.0981	0.0987	0.1500	0.1497

The stannic oxide found in 3 contained a trace of antimony. The oxide was converted into a sulpho-salt, and from its solution the metal was thrown down as stannic sulphide with dilute sulphuric acid. The solution obtained by dissolving the sulphide in concentrated hydrochloric acid was diluted, poured into a small carefully weighed platinum dish, and allowed to act on a roll of pure iron wire for several hours. The dish was covered with a clock glass and heated on the water-bath. A faint brown film which weighed 0.0003 grm. appeared on the dish. It dissolved readily in three drops of strong hydrochloric acid, and the solution diluted to about 5 cc. gave with hydrogen sulphide a red turbidity. After standing over night a tiny brown precipitate had collected on the bottom of the test-tube. The precipitate must have contained then some other sulphide in addition to that of antimony, for on this assumption alone can I account for the pronounced brown colour. The question whether antimonious sulphide dissolves in concentrated hydrochloric acid without the formation of traces of antimonious chloride is being investigated. According to Wittstein (*Pharm. Viertelj.*, xviii., 534) such traces are always present in the resulting solution. Scherer (*Zeit. Anal. Chem.*, iii., 206) and Classen (*Ber.*, xvi., 1061), however, state that during the reaction all the antimonious sulphide is converted into antimonious chloride.

Recently I have made some experiments to determine whether the separation of the two elements cannot be effected without the addition of sodium acetate to their hydrofluoric acid solution. It would appear that the Sb⁺⁺⁺ in such a solution, providing a moderate amount of free hydrochloric acid be present, is as completely precipitated by hydrogen sulphide as it is when the solution is first neutralised with caustic soda, the hydrofluoric acid and then the excess of sodium acetate added, and the gas introduced. True, I have as yet made no attempt to determine the amount of antimony present in the filtrate from the antimonious sulphide precipitated from such a solution, but the quantity must be practically negligible, for the figures for the tin and antimony found agree remarkably well with those representing the amounts taken.

The following experiment goes to show the degree of accuracy of this last mode of procedure:—0.4232 grm. of re-crystallised tartar emetic was placed in the large platinum dish and 25 cc. of the tin solution, 5 cc. concentrated hydrochloric acid, and 5 cc. 48 per cent hydrofluoric acid were added. The liquid was stirred with a platinum spatula until solution was complete, then diluted to 300 cc. and the hydrogen sulphide introduced. The antimonious sulphide was filtered off, dried, heated to blackness in a current of carbon dioxide, and weighed according to the directions already given. The tin in the filtrate was also determined as above described.

Found, 0.1563 grm. Sb = 36.94 per cent, and 0.1498 grm. Sn = 99.87 per cent.

The percentage of antimony in the sample of tartar emetic was next determined.

Tartar emetic taken.	Sb ₂ S ₃ found.	Sb found.
Grm.	Grm.	Grm.
0.51	0.2632	0.1880

0.1880 Sb = 36.86 per cent.

It may be well to state that solutions of tin and antimony containing hydrofluoric acid can be diluted indefinitely without any basic compounds separating out.

The method is being thoroughly examined, especially as regards its applicability to the analysis of alloys and metallurgical products containing tin and antimony.

THE OXIDATION OF PHENOL.*

THE EFFECT OF SOME FORMS OF LIGHT AND OF ACTIVE OXYGEN UPON PHENOL AND ANISOLE.

By H. D. GIBBS.

I HAVE shown (*Philippine Journ. Sci.*, Sec. A, 1908, iii., 361) that neither pure phenol, moist crystals, nor a solution of the crystals in water are affected by the intense sunlight of this locality when exposed in sealed glass tubes in atmospheres of nitrogen, hydrogen, or in case the starting material is a pale chamois colour, in case the starting material is a pale chamois colour, in case the starting material is a pale chamois colour.

Kohn and Fryer have exposed both dry and moist phenol in *vacuo*, and found the method for solution effect (*Journ. Soc. Chem. Ind.*, 1908, 415), conclude that the reactions of phenol are due to hydrogen peroxide oxidation, and that the presence of water, oxygen, and sunlight are all necessary factors, the absence of any one of which will prevent the reaction.

These writers, as I have shown (*loc. cit.*), are correct in their opinion that the cause of the red coloration is oxidation, and I have isolated the products to be expected from such a reaction, namely, quinone and catechol. Another substance which is probably formed during the reaction is quinol, and the presence of the condensation product, phenoquinone, is extremely probable.

Kohn and Fryer state (*loc. cit.*, 110):—"Since the coloration is always accompanied by the absorption of moisture, the presence of moisture is most probably intimately associated with the formation of the colour," and (*loc. cit.*, 111) "in the absence of moisture no coloration takes place."

Since writing the first article (*loc. cit.*), "The Compounds which cause the Red Colour in Phenol," this phase of the question has been investigated, and I find that these statements are not in accord with the facts. It is not surprising that Kohn and Fryer were led into this error, for the character of the sunlight available to them and the atmospheric conditions in their locality are hardly comparable with those in which I have worked in the Tropics.

Richardson says (*loc. cit.*, 415):—"Dr. Kohn also tells me that a degree of darkening in phenol, such as was obtained by me after three days' exposure in Clifton, England, could only be produced after many weeks under the conditions under which he has exposed it in Liverpool," and Kohn himself remarks (*loc. cit.*, 416) that in his own experiments the exposures have been made more under the conditions under which the usual reddening of phenol occurs, the samples being exposed in the south windows of a well lighted room.

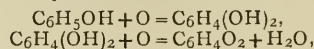
I am led to believe that active oxygen in any of its forms will react with pure dry phenol, and consequently produce the coloration. Kohn and Fryer (*loc. cit.*, 111) think that the oxidation of phenol goes on in the absence of light, and they make the following statement:—

"In respect to the action of light a series of experiments showed that the coloration is produced in the dark, although slowly, and therefore the light acts as an accelerator of the change only—an action of which there are many other instances."

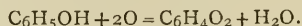
They made exposures of dry phenol in dry air to the light conditions in their locality, and found no coloration in seven months. I have, incidental to other work, exposed dry phenol in dry pure oxygen to the diffused light of this laboratory for several weeks, and moist phenol to moist atmospheric air in the dark at room temperature for two months without any appreciable coloration becoming visible. Nevertheless, it cannot be considered proved that there is no reaction between oxygen and phenol in the dark. In fact, it is probable, from considerations which will be advanced later, that a slow reaction takes place.

Hydrogen peroxide reacts readily, and I will show, in the experimental part of this paper, that dry ozone is very

reactive, either with the pure dry crystals or with melted phenol. The intimate association of water with the coloration, which Kohn and Fryer observed, is thus explained not as a compound necessary to the reaction, but as one of the products of the reactions:—



or—



There is no doubt, however, but that the rate of oxidation is more rapid in the presence of moisture. The separation, Chadwick, and Ramsbottom (*Journ. Chem. Soc. Trans.*, 1903, 1943) found that the presence of moisture that the result between carbon monoxide and oxygen in glance. If ultra-violet light increases the rate of the formation of carbon dioxide, and that while dry carbon dioxide is decomposed by the light, in the presence of moisture no decomposition could be detected. They conclude that in a photo-chemical reaction, the catalyst (moisture) exerts a marked influence in determining the mode of distribution of the energy amongst the molecules of the reacting substances.

Experimental.

Crystals of purest phenol were placed in a bulb tube and heated in an atmosphere of dry hydrogen until about 75 per cent volatilised. After cooling in the current of hydrogen this gas was replaced by dry atmospheric air which had been passed through a purifying chain. The tube was then carefully sealed and placed in the sunlight, at a temperature of about 30°. The crystals coloured slowly with liquefaction, until the entire mass had changed into a liquid of a deep red colour. The coloration was first noticeable in two hours, and liquefaction was complete after about five days, depending upon the quantity of phenol and oxygen present, the size of the tube, the quality of the glass, and some other factors. The experiment and results described were duplicated several times.

This work was then repeated with the utmost care and with an apparatus especially designed to eliminate all known sources of error. It permitted the double distillation of phenol over sodium in an atmosphere of dry pure hydrogen, and the condensation of any desired fraction in two tubes which could be sealed out of the apparatus independently of each other, the replacement of the hydrogen with purified dry atmospheric air or oxygen, and the treatment of one or both of the tubes with ozonised oxygen in the dark. During all of these operations there was no possibility for the entrance of moisture, for all of that portion of the apparatus between the extremities of the drying tubes at both ends of the chain was composed of glass vessels sealed in a continuous chain.

Description of Apparatus.

The gases employed, hydrogen, atmospheric air, and oxygen, were purified by passing through concentrated sulphuric acid, two tubes of calcium chloride, one tube of soda lime, a combustion tube filled with purified asbestos heated to redness, and then into the chain of apparatus shown in Fig. 1. Here the gases successively passed through a saturated solution of caustic potash, A, concentrated sulphuric acid, B, three tubes of phosphorus pentoxide held in place by plugs of glass-wool, C, D and E, an ozoniser of the Siemens (*Ann. d. Phys.*, 1857, cii., 120), form, F, and a tube of tightly packed glass-wool, G. The next portion of the apparatus consists of an arrangement of tubes and distilling flasks, enclosed in an asbestos oven, for the handling of the phenol, and the tube of phosphorus pentoxide, M, with its end dipping under mercury in the dish, N, to exclude moisture. All of the apparatus from A to N was connected by glass seals.

Drying the Apparatus and the Phenol.

After the complete chain was closed by glass seals, with the exception of the two extremities and the stopcock G,

* Contributions from Laboratory for the Investigations of Foods and Drugs, Bureau of Science, Manila, P.I. From the *Philippine Journal of Science*, vol. iv., No. 2.

the combustion tube was heated, and a slow current of hydrogen passed through for six hours. The portions of the apparatus enclosed in the asbestos oven, shown in Fig. 1 by the heavy lines, and also the tubes F and G were heated to 140° for four hours, after which the hydrogen current was stopped and the apparatus allowed to stand for ten days.

The phenol in this tube, K, coloured gradually when it was placed in the direct sunlight until the oxygen was practically all in combination. On breaking one of the points under water, the amount of oxygen which had combined was shown by the amount of water sucked in. Other tubes sealed in the same way were found to colour more or less rapidly, depending largely upon the temperature.

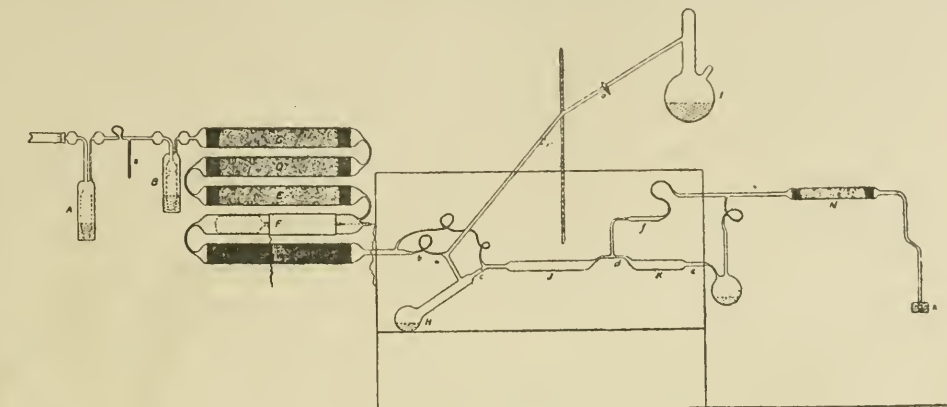


FIG. 1.

A pure sample of about 400 cc. of colourless phenol was employed as a starting material. It was distilled over a small piece of metallic sodium (see Note), and the middle fraction collected in a receiver arranged to exclude the light. After cooling, the flask was gently shaken, and the crystals which immediately formed represented only about one-half of the total mass, owing to the sudden rise in temperature due to the crystallisation of the super-cooled liquid. The melted portion was at once drained from the crystals. These were again distilled, and the middle fraction collected in the flask I through the side-tube. A small stick of metallic sodium was dropped in, the side-tube sealed, and a slow hydrogen current turned on. The purified sample was again distilled, the first fraction passing out through the tail of the stopcock g, and the middle fraction condensed in the flask H without stopping the distillation, by quickly turning the stopcock. The flask I was then removed by sealing the outlet tube below the stopcock g.

(NOTE.—The sodium employed was in the form of sticks enclosed in small glass tubing into which it has been introduced by melting *in vacuo*. Sections of the tube of the desired length were broken and immediately dropped into the distilling flask. By this means sodium of a comparatively pure quality, free from moisture and hydroxide, was obtained).

The asbestos oven was heated to from 160° to 180° in the steady current of hydrogen for two hours, the phenol partly vaporising and collecting in the receiver L. A small flame was then placed under the flask H, and the phenol boiled until about one-third had passed through the tubes J and K, and collected in H. The source of heat was removed from the oven, and the phenol condensed in the tubes J and K until they were about one-third filled. The whole apparatus was cooled in the current of hydrogen, and the distilling flask sealed out of the chain by closing the tubes at b and c. The residue in the distilling flask was colourless.

In order to change the gas in the apparatus and avoid the phenol coming in contact with oxygen which had not been heated (to eliminate the possibility of the presence of ozone) the outlet, a, was opened, and the hydrogen in the combustion furnace displaced by air. The combustion furnace was again heated, the outlet a sealed, and the hydrogen throughout the apparatus displaced by air. The tube K was removed by careful fusion at the points d and e.

When cooled by contact with broken ice, the coloration was only visible after several days' exposure to a bright sun. When the temperature was nearly that of the melting-point of phenol, the colour appeared in from fifteen minutes to one hour, probably because minute particles had been melted. Several tubes after exposure were tested for the presence of carbon dioxide by dipping the point under a clear solution of barium hydroxide, and allowing a small quantity of the solution to be sucked in. Small quantities of carbon dioxide were indicated in every case. About 2 grms. of pure phenol sealed, in a dry purified atmosphere containing a little more oxygen than atmospheric air, in a 200 cc. flask with two outlet tubes, was exposed to the direct sunlight for a month, and then tested for carbon dioxide by aspirating the gases through a barium hydroxide solution. All necessary precautions to avoid the introduction of the carbon dioxide of the atmosphere were taken. The tips of the outlet tubes of the flasks were not broken until the rubber tube connections were in place, a clear solution of barium hydroxide contained in a U-tube attached, and soda lime tubes and a wash bottle containing a concentrated solution of potassium hydroxide, to prevent the entrance of carbon dioxide, connected. A considerable amount of carbon dioxide was indicated by the heavy precipitate of barium carbonate.

After the tube K had been sealed off, the atmosphere in the apparatus was replaced by pure oxygen, the tube J being wrapped in black paper to exclude the light. No coloration of the phenol could be observed. The tube J containing the phenol crystals was then packed in broken ice, and the oxygen current ozonised by connecting the terminals of the ozoniser F with an induction coil. The reaction between the ozone and the cold phenol crystals was at first very slow, no appreciable coloration being visible for several hours. However, when it had begun, the action proceeded with increasing velocity, no ozone escaping from the reaction tube containing the phenol after the reaction was well under way. However, before that time a small quantity of super-cooled liquid phenol farther along in the apparatus, at the point f, coloured instantly upon the contact with the ozone, but none of the latter escaped at n, as was proved by repeated tests. In both cases the first colour was bright yellow; this colour gradually extended throughout the mass, and changed from yellow to pink, and finally to a dark reddish brown with gradual liquefaction of the crystals.

Another experiment was carried out in the same way, except that the phenol in the tube *j* was not cooled with ice, and was in the form of a super-cooled liquid. In this instance the phenol coloured with great rapidity, and no ozone escaped to the tube *f*. The liquid phenol in *f* in this experiment was not protected from the diffused daylight of the room, and nevertheless remained colourless after the exposure to the rapid current of oxygen throughout the entire experiment, which lasted for fourteen days. (The phenol was subjected to the action of the oxygen current for this length of time for the reason that the ozoniser was rather feeble, and produced only a small degree of ozonisation). On bubbling the oxygen escaping at *N* through a potassium iodide-starch solution, no coloration was produced, showing that the ozone was entirely removed by reaction with the phenol. Carbon dioxide is given off in considerable quantities during the reaction.

The tube *j* was finally opened and a study of the reaction products made. The reddish brown liquid was shaken with water, the insoluble portion separated, and the aqueous solution extracted repeatedly with chloroform and ether. These extracts were found to contain considerable quantities of unchanged phenol, small amounts of quinone and catechol, and considerable amounts of quinol.

The aqueous solution contained an acid which was volatile with steam, reduced ammoniacal silver solution and mercuric chloride, was precipitated by calcium hydroxide, and on boiling precipitated calcium oxalate. It gave an orange-yellow precipitate with phenylhydrazine in the cold (E. Fischer, *Ber.*, 1884, xvii., 577). This precipitate on purification and re-crystallisation formed yellow crystals. Even though an insufficient quantity of the phenylhydrazine compound was obtained for an analysis, it is reasonably safe to assert that the acid in aqueous solution was glyoxylic acid.

Several experiments were completed in the same manner with the difference that the issuing gases were passed through $N/5$ solutions of barium hydroxide. The following was the result:—

	Grms.
Carbon dioxide evolved	0.11
Weight of the mixture in the tube <i>j</i> when the evolution of carbon dioxide had practically ceased . .	3.00
Acidity of aqueous extract was equivalent to 18 cc. $N/10$ = glyoxylic acid ($CHO \cdot COOH$) equivalent to	
4.4 per cent of the residue	0.13
Chloroform extract	0.64
Ether extract	0.23

The chloroform and ether extracts were dried in a vacuum desiccator with the loss of considerable of the products. The principal loss in weight was due to phenol vaporised.

Two grms. of another residue, on distillation with steam, gave an acid distillate equivalent to 16 cc. $N/10$ alkali which, calculated as glyoxylic acid, equals 5.9 per cent.

(To be continued).

THE COWPER-COLES ENGINEERING COMPANY'S EXHIBIT AT THE WHITE CITY.

AMONG the interesting items exhibited by this Company, we may draw our readers' attention to a number of specimens and working models of apparatus for coating steel and iron with zinc by the regenerative process. The advantages of this process over the hot galvanising process is that there is no reduction of tensile strength; for a given quantity of zinc a better protection is obtained, screws, pipes, bolts, nuts, &c., can be coated with zinc without having the threads re-cut, which is necessary when the old molten process is employed.

Specimens, working drawings, and illustrations of plant for the direct production of copper sheets, tubes, and wire

by the Cowper-Coles centrifugal electrolytic process. This process enables copper sheets and tubes to be made direct from crude copper in one operation without smelting. In the old process a large amount of energy is applied to a mass of metal in a short time, as in the case of rolling; in the new process a comparatively small amount of energy is required, each molecule being burnished as deposited on a revolving mandrel, and it has been found that there is a critical speed for every separate metal to obtain the best results. The material produced by the centrifugal process has a much higher strength than that obtained by the old process.

The method of producing wire by the Cowper-Coles process is based on the fact that if metals are cast in a right-angle mould a weak line of cleavage is formed.

It was discovered by Mr. Cowper-Coles that a similar result could be obtained in electro-deposited copper; the practical application consists of making a fine V-shaped spiral scratch around the mandrel, on which the copper is deposited; this can be unwound in the form of a strip, in some cases four miles in length.

Metallic Parabolic Reflectors for Searchlights.—Mr. Cowper-Coles's latest invention in connection with this branch of electro-metallurgy consists in the production of metallic mirrors electro-deposited, with alternate bands of gold and silver.

It has been found that a gold mirror gives a far more penetrating beam of light than that reflected from a silver mirror. The combination of the two metals therefore gives a beam which is very penetrating, and yet retains the valuable property required for searchlights for military purposes, viz., the dazzling effect.

For motor-car head-lights, gold mirrors are supplied; they show up distant objects very clearly, and do away with the dazzling effect.

A number of interesting metals which have been treated electrolytically are also exhibited—chromium, cobalt, platinum, palladium, and iridium; also specimens of electro-deposited alloys, such as cadmium and silver and brass.

PROCEEDINGS OF SOCIETIES.

AMERICAN CHEMICAL SOCIETY.

DETROIT MEETING, June 29th to July 2nd, 1909.

THE meeting of the American Chemical Society at Detroit was more largely attended than any summer meeting in its history, and all the members returned to their homes enthusiastic over the work accomplished by the various Divisions of the Society.

Meetings were held by the Division of Industrial Chemists and Chemical Engineers, the Division of Physical and Inorganic Chemistry, the Division of Organic Chemistry, the Division of Fertiliser Chemistry, and the Division of Agricultural and Food Chemistry, and by the Sections of Biological Chemistry and Pharmaceutical Chemistry, and the Section of Chemical Education. In all 186 papers were presented.

Besides the reading of the various papers the points of special interest were the largely attended meetings of the Division of Industrial Chemists and Chemical Engineers, which are continually growing in enthusiasm, and where representatives were present from all parts of the country. Perhaps the "experience meeting" before this Division on Friday morning was the most entertaining feature of their programme, for many ideas of value were brought out and the discussion was general. It seemed as if almost every member had some interesting fact which bore upon the experience of others, and the hour for adjournment was delayed to the very latest possible moment on account of the keen interest aroused. It is quite noteworthy that the

mantle of secrecy which has enveloped so many of the chemical industries and industrial chemists in the past appears to be falling away under this enthusiasm, and both the industries and the industrial chemists themselves find that they gain more than they lose thereby. In this connection it might be added that a considerable number of chemical corporations are joining the Society as such, and are heartily entering into the spirit of progress with which the Society is so thoroughly imbued.

The Section of Pharmaceutical Chemistry, which held its first meeting in Baltimore, was surprisingly well attended at Detroit with representative pharmaceutical chemists from various sections of the country. The chief matter of importance before the Section was the question of the advisability of forming a Division of Pharmaceutical Chemistry. After the matter was discussed by almost everyone present, and many letters were read from pharmaceutical chemists, it was unanimously voted to request the Council to establish such a Division, and a strong organisation was formed with Prof. A. B. Stevens, of Ann Arbor, as Chairman; B. L. Murray, Secretary; J. P. Remington, E. Kremers, and J. M. Francis, Executive Committee.

The social features of the meeting were many. A complimentary Smoker was given by the Society of Detroit Chemists to the visiting chemists on Tuesday evening, and a banquet on Thursday night. On Wednesday afternoon the chemists were the guests of Parke, Davis, and Co., and visited the works of this well-known firm, were entertained there at dinner, and were given an evening boat-ride on the Detroit River and Lake St. Claire before returning. Thursday was spent in Ann Arbor as the guests of the Regents of the University of Michigan, and three papers of general interest were there presented in general session. The rest of the day was turned over to the Section of Chemical Education, where papers dealing with methods of instruction were read. During the day the members visited the new laboratories of the University of Michigan, and were entertained at luncheon through the courtesy of the Regents.

Many manufacturing works and chemical establishments were opened to the visitors in Detroit, among which may perhaps be especially mentioned Acme White Lead and Colour Works, Detroit Salt Company, Hiram Walker and Sons, Hoskins Manufacturing Company, and the various automobile factories which have so greatly added to the industrial life of Detroit.

A steadily increasing number of members of the Society are making it a point to attend the meetings, and it is interesting to note that more and more chemical corporations are appreciating the value of these meetings to their chemists, and are insisting upon their attendance, in most cases bearing all the expenses of the trip.

The American Chemical Society now has over 4400 members, which are rapidly increasing in number, largely due to the fact that each member receives all three of its publications: *The Journal of the American Chemical Society*, *Chemical Abstracts*, and *The Journal of Industrial and Engineering Chemistry*.

CHARLES L. PARSONS, Secretary.

NOTICES OF BOOKS.

Third Report of the Wellcome Research Laboratories at the Gordon Memorial College, Khartoum. ANDREW BALFOUR, Director. London: Baillière, Tindall, and Cox. 1908.

HITHERTO the reports of the Wellcome Research Laboratories have been given gratuitously to Government departments, medical and sanitary institutions, &c., but the director considers that the time has now come to give a wider public the opportunity of becoming familiar with the work that is being done in the laboratories, and accordingly the third volume, dealing with the progress down to 1908, is to be sold at a cost of 10s. 6d. Many scientific men

and doctors who are interested in tropical research will be glad to read an account of the advances which have been made in bacteriology and physiology, and they will recognise that the college is doing work which is of the greatest importance both from a practical standpoint and also as adding to purely scientific knowledge. The report of the work done in the chemical section deals with the analyses which have been performed of waters of various origins, and also of feeding substances, and contains an account of an investigation of the chemical nature and properties of Sudanese gums. The whole book is excellently illustrated, and is a record of a marvellous amount of highly skilled and patient work on the part of the staff attached to the laboratories.

Laboratory Manual of Dyeing and Textile Chemistry. By J. MERRITT MATTHEWS, Ph.D. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1909.

IN this book every possible device is employed to impress upon the student's memory the actual results obtained in his practical work on dyeing, and to help him to interpret them correctly. Thus nearly eight hundred questions on the subject of the practical work are included, most of them relating directly to the experience the student has gained in working through the tests described, although in a few cases it will be necessary to fall back upon a previous knowledge of chemistry in order to answer them correctly. It is suggested that the course of laboratory work given in the book should be worked through in a year, but it hardly seems possible that this could be done satisfactorily, and probably a much longer time could profitably be given to it. General methods of dyeing different materials, the testing of fastness and the chemical reactions of dyestuffs are all adequately treated, and if the student follows out all the directions he will prepare nearly five hundred samples, showing the effects of dyes of all classes upon various materials under different conditions. The analysis of textile fabrics by chemical methods is briefly treated, and many numerical tables for shortening calculations, together with useful data, are given in an appendix.

Chemical Industry on the Continent. A Report to the Electors of the Gartside Scholarships. By HAROLD BARON, B.Sc. Manchester: The University Press. 1909.

THE issue of the Gartside Reports by the scholars of the University of Manchester shows how valuable the Gartside scholarships are in widening the knowledge of English students with regard to commerce and industries, especially those of foreign countries. The author of this report has studied more particularly dyeing and the manufacture of aniline dyes in Belgium, the North of France and Germany, and he has been able to collect a good deal of information relating to the practice in different works. Other industries are also considered in the report which may profitably be studied by students of science and economics. The accounts of the various industries are not highly technical, but they reveal the author's fitness for industrial research, and his future contributions to the science in which he is specially interested should be all the more valuable owing to the opportunity he has had of gaining a first-hand knowledge of the industrial conditions of other countries.

Laboratoriumsbuch für die Industrie der verflüssigten und Komprimierten Gase. ("Laboratory Book for the Liquid and Compressed Gases Industry"). By Dr. KARL URBAN. Halle-a-S.: Wilhelm Knapp. 1909.

THIS book gives in concise form details of methods of testing the most important liquefied and compressed gases which are used commercially. The tests described are those which are usually employed technically, and hence they may be regarded as standard methods which can be relied upon to give directly comparable results. The gases treated include ammonia, chlorine, carbon dioxide, oxygen, hydrogen, and sulphur dioxide, and in each case tables are

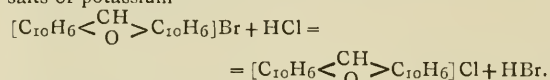
given showing the physical constants of the substance, the specific gravity and tension being given within wide limits of temperature. The analysis of the substance for impurities is given full consideration, the different apparatus used being described in detail and illustrated. In some cases, for instance in that of CO_2 , the standards to which the commercial substance should attain are stated.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

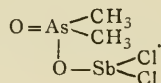
Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlviii., No. 24, June 14, 1909.

Metallic Character of an Organic Radical.—R. Fosse.—The monochlor and monobrom derivatives of dinaphthopyrane, $\text{C}_{10}\text{H}_6 < \text{CH} > \text{C}_{10}\text{H}_6$, which the author discovered and called salts of pyryl, have very peculiar properties, which mark them out from other organic haloids. Thus with hydrides they give the same reactions as the salts of potassium—

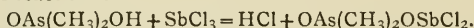


Conversely, hydrobromic acid transforms the chloride of pyryl into the bromide, setting free hydrochloric acid. In acetic acid solution the salts of pyryl behave like potassium salts towards picric acid, a picrate is deposited, and the acid of the original salt is set free. Sulphuretted hydrogen precipitates as sulphide the chloride, bromide, and sulphate of pyryl in mineral or organic acids.

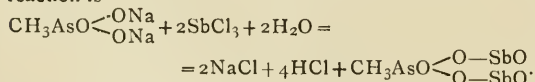
Action of Cacodylic and Methylarsinic Acids on Antimony Trichloride.—L. Barthe and A. Minet.—Cacodylic acid reacts on antimony trichloride in concentrated solution to give a dichlorcacodylate of antimony of formula—



The reaction is—



The cacodylate is insoluble in water, but dissociates rapidly in boiling water. It may be crystallised from 95 per cent alcohol containing 1 per cent HCl. When deliquescent antimony trichloride is added to a boiling solution of methylarsinic acid saturated with sodium bicarbonate an apparently amorphous precipitate is obtained. After being kept for one or two hours on the water-bath the compound crystallises. Its formula is $\text{CH}_3\text{AsO} < \text{O}-\text{SbO} > \text{O}-\text{SbO}$, and the reaction is—



Aromatic Alcohols and Hydrocarbons derived from Fenone.—J. Leroide.—Fenone gives with benzene magnesium derivatives addition products which are insoluble in ether and in hydrocarbons. When treated with water these derivatives give fenone and the hydrocarbon corresponding to the magnesium compound employed. The following compounds have been prepared thus:—
 $\text{C}_6\text{H}_5\text{MgBr} \cdot \text{C}_{10}\text{H}_{16}\text{O}$; $\text{CH}_3-\text{C}_6\text{H}_4-\text{MgBr} \cdot \text{C}_{10}\text{H}_{16}\text{O}$;
 (1) (2)
 $\text{CH}_3-\text{C}_6\text{H}_4-\text{MgBr} \cdot \text{C}_{10}\text{H}_{16}\text{O}$. When heated for some time in presence of a large amount of solvent these compounds are transformed into magnesium derivatives of tertiary alcohols.

UNIVERSITY OF GLASGOW.

SESSION 1909-10.

[The Classes for Women are partly conducted in a separate building (Queen Margaret College), and are taught by Professors of the University and other Lecturers appointed by the University Court. For details see separate advertisement].

The MEDICAL SESSION will be opened on MONDAY, the 11th OCTOBER, 1909.

WINTER COURSES.

Zoology, Elementary, 9 a.m.; and Zoological Laboratory, Elementary, 11 a.m. or 3 p.m.—Professor GRAHAM KERR, M.A., F.R.S.
 Chemistry, 10 a.m.; and Chemical Laboratory, 10 a.m. to 4 p.m.—Professor FERGUSON, M.A., LL.D., F.S.A.
 Organic Chemistry, Elementary.—T. S. PATTERSON, Ph.D., D.Sc.
 Anatomy, Junior, 11 a.m.; Senior, 1 p.m.; and Practical Anatomy, 9 a.m. to 4.45 p.m.
 Physiology, 12 noon; Practical Physiology; and Physiological Laboratory.—Professor NOEL PATON, B.Sc., M.D., and Assistants.
 Physiological Chemistry.—E. P. CATHART, M.D., D.Sc.
 Physiological Physiology.—HENRY J. WATT, M.A., Ph.D.
 Materia Medica and Therapeutics, 11 a.m.; and Pharmaceutical Laboratory.—Professor STOCKMAN, M.D.
 Pathology, Systematic, 3 p.m.—Professor MUIR, M.A., M.D.
 Surgery, 12 noon.—Professor Sir WILLIAM MACEWEN, M.D., LL.D., F.R.S.
 Midwifery, 2 p.m. Professor MURDOCH CAMERON, M.D.
 Practice of Medicine, 11 a.m.—Professor GEMMELL, M.D.
 Clinical Medicine, 9 a.m.—Professor GEMMELL, M.D.
 Clinical Surgery, 9.15 a.m.—Professor Sir HECTOR C. CAMERON, M.D., and Professor Sir WILLIAM MACEWEN, M.D., LL.D., F.R.S.
 Public Health, 12 noon, four days weekly; Public Health Laboratory, 10 a.m. to 4 p.m.—Professor GLAISTER, M.D., D.P.H. (Camb.).
 Ear, 4 p.m., Monday (University); Practical Instruction as may be arranged.—THOMAS BARR, M.D.
 Throat and Nose, 4 p.m., Thursday (University); Tuesday or Friday (Western Infirmary).—JAMES WALKER DOWNIE, M.B.

SUMMER COURSES.

Commencing on TUESDAY, APRIL 19th, 1910.

Physics, 11 a.m.—JAMES G. GRAY, D.Sc.
 Practical Physics, 9 to 11 a.m., or 2 to 4 p.m.—Professor GRAY, M.A., LL.D., F.R.S.
 Botany, 8 a.m.; and Botanical Laboratory, 9 a.m. to 4 p.m.—Professor BOWER, Sc.D., F.R.S.
 Clinical Medicine, 9 a.m.—Professor GEMMELL, M.D.
 Clinical Surgery, 9.15 a.m.—Professor Sir HECTOR C. CAMERON, M.D., and Professor Sir WILLIAM MACEWEN, M.D., LL.D., F.R.S.
 Chemical Laboratory, 10 a.m. to 4 p.m.—Professor FERGUSON, M.A., LL.D., F.S.A.
 Organic Chemistry, Elementary.—T. S. PATTERSON, Ph.D., D.Sc.
 Practical Anatomy, 9 a.m. to 4 p.m.
 Embryology, 11 a.m.; and Embryological Laboratory, 9 a.m. to 4 p.m.—JAMES F. GEMMILL, M.A., M.D.
 Applied Anatomy, 1 p.m., Monday, Wednesday, Friday.—ROBERT KENNEDY, M.A., D.Sc., M.D.
 Practical Pharmacy, 12 noon.—Professor STOCKMAN, M.D.
 Practical Physiology, 9 to 11 a.m.; and Physiological Laboratory.—Professor NOEL PATON, B.Sc., M.D., and Assistants.
 Medical Jurisprudence and Public Health, 11 a.m.; and Public Health Laboratory.—Professor GLAISTER, M.D., D.P.H. (Camb.).
 Practical Pathology, 1 to 3 p.m.—Professor MUIR, M.A., M.D.
 Operative Surgery, 12 noon, with practical work at other hours.—Professor Sir WILLIAM MACEWEN, M.D., LL.D., F.R.S.
 Diseases of Women, 2 p.m., Tuesday, Thursday, and Friday.—Professor MURDOCH CAMERON, M.D.
 Insanity, 12 noon, Wednesday (University); 10 a.m., Saturday (Gartnavel).—LANDEL R. OSWALD, M.B.
 Ear, 4 p.m., Monday (University); Practical Instruction as may be arranged.—THOMAS BARR, M.D.
 Throat and Nose, 4 p.m., Thursday (University); Tuesday or Friday (Western Infirmary).—JAMES WALKER DOWNIE, M.B.

Western Infirmary.—This Hospital, near the University, contains over 500 Beds for Medical and Surgical Patients, including Wards for Skin Diseases, and two for Diseases peculiar to Females.

Degrees.—Four Medical Degrees are conferred under the new regulations, viz., Bachelor of Medicine (M.B.) and Bachelor of Surgery (Ch.B.), which must be taken together; Doctor of Medicine (M.D.), and Master of Surgery (Ch.M.); all of which are recognised by the Medical Acts as qualifying for Practice throughout the British dominions. The Degrees of B.Sc. and D.Sc. in Public Health, and of B.Sc. in Pharmacy, are also conferred.

Fees.—The Fee for each Systematic Class is, as a rule, £4 4s. The Fee for M.B. and Ch.B. is £23 2s.; for M.D., £10 10s.; for Ch.M., £10 10s.; for B.Sc., £6 6s.; for D.Sc., £10 10s.

Bursaries.—Bursaries to the annual amount of upwards of £1000 are restricted to Medical Students, whilst Scholarships and Fellowships to the amount of upwards of £1800 may be held by Medical Students who have gone through the Arts Course.

Full particulars as to the Course of Education and Examination required for the Degrees, and the Preliminary Examination required to be passed by Students before beginning Medical study, will be found in the University Calendar (by post 3s. 4d.); or a Syllabus of the Regulations, Fees, &c., may be obtained by applying to Mr. W. INNES ADDISON, Assistant Clerk of Senate.

THE CHEMICAL NEWS.

VOL C., No. 2594.

EUROPIUM, GADOLINIUM, TERBIUM, NEOYTTERBIUM, AND LUTECIUM.

By Dr. G. URBAIN,
Professor of Chemistry at the University of Paris (Sorbonne).

It is impossible for me to enter into full particulars of the researches which have engaged my attention for about fifteen years, and I must limit myself to giving a review of them. I shall endeavour to explain as simply as possible the conceptions which have been my guide and the principal results which I have obtained.

Fifteen years ago, especially after the principal researches of Sir William Crookes, to whose attainments and inaptitude I wish to testify, although our conclusions are diametrically opposed, the group of the rare earths, and more particularly the yttrium earths, was supposed to be composed of an infinite number of substances. It seemed as if the idea of isolating each one would have to be abandoned, and that we should have to be contented with observing the new characters which could serve to define the new elements.

Any research aiming at the determination of the individuality of an element consists of a chemical part, relating to the separation of the substances, and a physical-chemical part, relating to the measurement which enable us to identify the elements.

To separate elements which possess chemical properties as similar as those of the rare earths we can only employ methods which recall the fractional distillations used in organic chemistry to separate substances of the same chemical function. But as the rare earths give volatile compounds only at practically unattainable temperatures, we are forced to fall back either on fractional precipitations or fractional crystallisations.

I have given up as impossible fractional precipitations owing to the amount of manipulation they necessitate, and I have performed chiefly fractional crystallisations, using preferably very soluble salts. For these operations, which must be repeated thousands of times before they give satisfactory results, the most convenient salts, for practical reasons, are those which dissolve in their water of crystallisation, such as the nitrates, for instance. However, it must be ascertained for certain whether the proposed method is efficacious.

To avoid dust it is best to perform the crystallisations in flasks. Good glass, such as Jena or Krasna glass, must be chosen. The flasks must not be more than half full to allow of dilatation and to avoid breakages. After each crystallisation the mother-liquors must be reduced to a minimum. The only necessary operations are decantation, solutions, and concentration. They are very simple, and the last can be performed in series by heating a great number of flasks simultaneously upon a heated metallic plate. This method has previously been worked out by E. Demarçay.

At first large flasks were used, but it is dangerous to employ flasks containing more than 1 litre. At the end of the research quite little ones were used. Those in which I obtained lutecium had a capacity of about 20 cubic mm. At one time I had in my laboratory more than 300 flasks in which crystallisations were being carried out. All underwent a series of crystallisations in half-a-day. I and my assistants could perform two series of crystallisations daily, and the total of all the crystallisations exceeded three hundred thousand.

The following is a short description of the *modus operandi*. Suppose that the fractionation which is to isolate a sub-

stance comprises fifteen fractions, numbered in order of solubility. No. 1 is the least soluble and No. 15 the most soluble. The mother-liquors from No. 15 are decanted into a sixteenth flask, and the mother-liquors from No. 14 are decanted into flask 15. The crystals of flask 15 are then dissolved in the mother-liquor of flask 14, and so on. Pure solvent is constantly put into fraction 1, which finally disappears. The first fraction is then No. 2, but when flask 16 has received enough mother-liquors for the contents to crystallise, a seventeenth flask is employed. In this way the number of flasks remains constant. It is best, in order to avoid useless concentrations, to make all the fractions equal in volume—the number of fractions necessary depends on the efficacy of the method, and is inversely proportional to it.

The substances must have been previously divided into groups. In my principal work on the earths of monazite which required 500 kg. of original material, the first rough treatments were carried out in a manufactory. It was the almost unknown yttrium earths which interested me, and they had to be separated from the considerable quantities of the earths of the cerium group—cerium, lanthanum, praseodymium, neodymium, and samarium. Moreover, the yttrium earths contain not less than 80 per cent of yttrium which has to be removed. The necessity of starting with such quantities of material is seen when it is remembered that some of the earths—europium, terbium, lutecium—are in a very dilute state in the rare earths themselves. According to my calculations the yttrium earths of monazite contain less than a two hundred thousandth of europium, and yet by continuing the fractionation systematically I have succeeded in isolating this europium nearly quantitatively.

This part of the work, which was carried out in collaboration with H. Lacombe, was the key to the rest. We finally effected a complete separation of europium and samarium as follows:—We found that bismuth nitrate gives with the nitrates of the magnesium series salts which are completely isomorphous with the double nitrates formed by the nitrates of the rare earths with the nitrates of the magnesium series $2M(NO_3)_3 \cdot 3Mg(NO_3)_2 \cdot 24H_2O$; M is either bismuth or one of the rare earths Ce, La, Nd, Pr, Sm, Eu, Gd, Tb. . . .

After some search we found that as regards the solubility of its double nitrate Bi comes between Sm and Eu.

Isomorphism, which is the chief obstacle in the separation of the rare earths, has thus in this case enabled us to separate them.

To the mixtures in the state of magnesium nitrates was added a large excess of bismuth magnesium nitrate. Then they were systematically fractionated. Ce, La, Pr, Nd, Sm crystallise first, then bismuth, leaving Eu, Gd, &c., to the end. When the middle fraction only contains bismuth the samarium is separated quantitatively from the europium. It is only necessary to eliminate the Bi, which can easily be done with H_2S ; the rare earths are not precipitated by this reagent.

Thus bismuth acts as the separating element. If there were other common elements isomorphous with the rare earths this method could be generalised. Unfortunately bismuth is unique in this respect, and it is a remarkable fact that all the salts of bismuth which are isomorphous with those of the rare earths—and they are numerous—occupy as regards their solubility the same position in the series, so that the idea of cutting the series in the same way at some other point has not much chance of success.

This fact seems to me to point to a great natural law relating to the solubility of the elements of the same series. I have frequently observed that whatever the method of crystallisation employed the rare earths arrange themselves in the same order (see accompanying table).

If yttrium is excepted this is the order of increasing atomic weight. This law has been overlooked until my researches because with certain salts the series turns back on itself, like the dispersed rays of the spectrum in the base of abnormal dispersion.

Lanthanum	La =	139.0
Cerium	Ce =	140.25
Praseodymium	Pr =	140.6
Neodymium	Nd =	144.3
Samarium	Sm =	150.4
(Bismuth)		
Europium	Eu =	152.0
Gadolinium	Gd =	157.3
Terbium	Tb =	159.2
Dysprosium	Dy =	162.5
Holmium	Ho =	$> 162.5 < 167$
Yttrium	Y =	89.0
Erbium	Er =	167
Thulium	Tu =	168.5
Neoytterbium	Ny =	172
Lutecium	Lu =	174

I have succeeded in separating from one another the elements in the middle of the series Sm, Eu, Gd, Tb, Dy by crystallising different salts, the most important of which are the ethyl sulphates, the double nitrates of the magnesium series, and the simple nitrates with 5 molecules of water. I have not only been able to define them exactly by the description of their spectra and the determination of their atomic weights, but I have also established the invariability of their properties, and I have shown that no other element can exist among them. Taking the yttrium series at the other end, I have recently shown that ytterbium is a mixture of variable atomic weight, and I have separated from it the new element lutecium. Six weeks after me Auer published numerical results agreeing with mine.

The following is a short summary of the principal results which I have contributed to the chemistry of the rare earths:—The discovery of two elements, lutecium and neoytterbium, and the complete description of four others, europium, gadolinium, terbium, and dysprosium. This research has led to the appearance in the International Table of Atomic Weights of the elements europium, dysprosium, lutecium, and neoytterbium, which have thus been officially recognised in international science.

The foregoing research might strictly pass for pure chemistry. But the methods of investigation of physical chemistry are of such importance in this work that I thought that it was worth while to describe them in the Physical Chemistry Section of the International Congress of Applied Chemistry.

It is not sufficient to fractionate the mixture and to determine the atomic weights in order to decide such a question as this. This would give only a first approximation, because two neighbouring elements have sometimes almost identical atomic weights. Moreover, the atomic weight is insufficient as the only characteristic.

Acting on this principle, I have always endeavoured to carry out very exact measurements. Taking for the abscissæ the numbers of the fractions and for the ordinates the atomic weights, the curves obtained at the beginning of a fractionation are continuous, and regularly ascend or descend. When the separations are more advanced we see in the curves indications of horizontal regions which subsequently become more distinct. When several consecutive fractions have the same atomic weights within the limits of errors of measurement, these horizontal parts generally correspond to pure substances. But they may also correspond to mixtures. In fractional distillations there are liquid mixtures which distil at a constant temperature; and in fractional crystallisations we come across mixtures which cannot be separated. I have given some examples of such mixtures, and have put forward a theory to explain the phenomenon.

I have studied systematically the different spectral characters of the horizontal parts of constant atomic weight, examining each characteristic in the successive fractions. At first I met with various difficulties.

The rare earths, like all the chemical elements, give, in general, three kinds of spectra:—Emission spectra, absorption spectra, phosphorescence spectra.

The data of different authors were very incomplete and often contradictory. Generally speaking, each author had limited himself to the observation of one single kind of spectral character, and attributed to a new element any new spectral character which he observed. One single element might give these three kinds of spectra, and thus each element might be discovered at least three times. The chemistry of the rare earths was thus encumbered with elements provisionally denoted by the letters, X, Y, Z, G, . . . —Δ, I, ζ, The Greek and Roman alphabets were inadequate, and the impression was given of a swarm of inaccessible elements. Moreover, it has long been known that the spectrum of an element is never invariable; the intensity either of the bands or of the lines may change appreciably under the influence of various agents, so much so that it almost seemed as if the different bands of a spectrum are characteristic of distinct elements. If, moreover, we notice that the spectra of the rare earths are always very rich and sometimes extremely sensitive, we can form an approximate idea of the difficulty of the problem.

Each spectrum has been subjected to a systematic examination, and I have had to study the different methods which have been suggested and which often give very different results—for an emission spectrum, for instance. Arc spectra differ from spark spectra. Spark spectra may acquire very different appearances according to the capacity and the self-induction of the exciting circuit. Finally, when a substance is present in traces its spectrum generally differs from the spectrum given by large quantities of it.

Absorption spectra vary with the acidity, the concentration of the solution, and the temperature.

However, the emission and absorption spectra have an intensity which is practically proportional to the masses which give rise to them, only emission spectra are more sensitive than absorption spectra. Hence we can see if two spectra (one emission and the other absorption) belong to the same element. In consequence of differences of sensibility they undergo the same displacement above and below the horizontal region of constant atomic weight, along which they remain the same, exhibiting their maximum brightness.

It is different with phosphorescent spectra. This part of my spectrographic work was the most tedious.

Phosphorescence is a Property of Diluted Matter.—It is the mixtures with some hundredths of active matter—phosphorogen as it is called—which, in a vacuum and under the influence of the cathode rays, become the most luminous.

Above or below this optimum, whether the proportion of phosphorogen increases or decreases in the mixture, the phosphorescence is less bright. It generally disappears considerably before pure substances have been obtained.

I have verified this fact by diluting non-phosphorescent pure substances in other pure substances also non-phosphorescent. The analytical work was thus duplicated by synthetical experiments, which completed it.

This systematic study has shown that not only the cathode phosphorescence of an element diluted in increasing proportions in another passes through a maximum, but also that most of the bands of the same spectrum admit of luminous optima.

We may sum up the law which regulates the phosphorescence of the solid mixtures as follows:—

In any binary phosphorescent system in which the relative proportions of phosphorogen and diluent are altered, it has been shown that—

1. Each phosphorescence band passes through an optimum.
2. The optima of different bands do not necessarily coincide although they always correspond to relatively small proportions of phosphorogen.

This law gives the key to the phenomena which have been observed, and which may be summarised as follows:—

1. The horizontal regions representing pure substances are not phosphorescent.

2. The intermediate mixtures are generally phosphorescent, and from one fraction to another the colour and the spectrum of the phosphorescence undergo regular progressive modifications.

These changes lead to the supposition of a separation of several phosphorescent rare earths, but this illusion is destroyed by synthetical experiments made with pure substances mixed in different proportions, for we cannot admit that by mixing two substances we could thus have separated the constituents.

By a very large number of crucial experiments I have established the correctness of these views, the proof being rigorous and one which seems to me irrefutable. They are in contradiction to the so-called interpretation which, under the name of the "Theory of the Meta Elements," Sir William Crookes has given of the magnificent phenomena the discovery of which is due to him.

My experiments have for the most part confirmed the results obtained by Sir William Crookes. By them the chemistry of the rare earths has gained in simplicity what it has lost in charm.

The experiments which I have described, dwelling only on the main principles, have led me to the following conclusions:—

I. The elements $S\delta$ of Sir William Crookes, $Z\zeta$ and $Z\epsilon$ of M. Lecoq de Boisbaudran are actually identical with Demarçay's europium. This element possesses an emission spectrum, an absorption spectrum, a phosphorescence spectrum (which appears only when the derivatives of europium are mixed in suitable diluents). The atomic weight of europium is $Eu = 152.0$.

II. The element victorium of Sir William Crookes is identical with gadolinium. This element also exhibits the three sorts of spectra. Its atomic weight is $Gd = 157.3$.

III. The elements Γ of Demarçay, $Z\beta$ and $Z\delta$ of Lecoq de Boisbaudran, $G\beta$, ionium, and incognitum of Sir William Crookes are identical with terbium, the existence of which was foretold by Mosander, although it was not isolated and described till sixty years later. Its atomic weight is $Tb = 159.2$.

IV. The elements Δ of Demarçay, $Z\alpha$ and $Z\gamma$ of Lecoq de Boisbaudran, $G\delta$ of Sir William Crookes, X_2 of Exner and Haschek are identical with Lecoq de Boisbaudran's dysprosium. Its atomic weight is $Dy = 162.5$.

V. Marignac's ytterbium is a mixture of at least two elements. I have found that the atomic weight of one is about 174, and I have defined it by this and by a line and a band spectrum. This is lutecium. I have called the residue of the old ytterbium neoytterbium. Its mean atomic weight is 172, but I have not yet obtained it constant, and I have observed such variations in its band spectrum that I am inclined to think that it is itself a mixture of two elements.

Pseudomorphine.—Gabriel Bertrand and V. I. Meyer. —The authors have shown that pseudomorphine is a derivative of two molecules of morphine, each of which loses one atom of hydrogen. The two morphine residues are apparently united by their carbons. Thus when morphine is transformed into pseudomorphine oxidation occurs, the reaction being to a certain extent similar to that which occurs when laccase acts on guaiacol. From the strong optical activity of the molecule of pseudo-

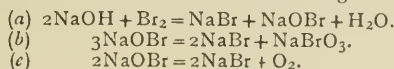
morphine the formula must be $C_{17}H_{18}NO_3$, and

$$\begin{array}{c} C_{17}H_{18}NO_3 \\ | \\ C_{17}H_{18}NO_3 \end{array} \quad O_3NH_{18}C_{17}$$
 of the symmetrical — *Comptes Rendus*, cxlviii., No. 25.

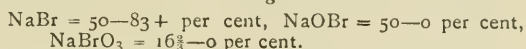
ANALYSIS OF MIXTURES OF HALOGEN ACIDS.

By WILLIAM M. DEHN.

In an alkaline sodium "hypobromite solution," prepared by adding bromine to an excess of caustic soda, the bromine is present in three different forms, namely, sodium bromide, sodium hypobromite, and sodium bromate. For a greater or less time after preparing such a mixture, the percentages of these three substances vary progressively, owing to the combined effects of the following reactions:—

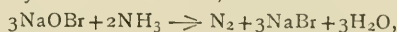


Whereas the main reaction (a) is immediate and quantitative, the other reactions proceed more or less slowly, owing to the varying influences of heat, light, decrease of alkalinity, &c. (Gay Lussac, *Ann.*, xliii., 153; *Comptes Rendus*, xiv., 927; Foerster and Jorre, *Journ. Prakt. Chem.*, lix., 53; Skrabal, *Monatsh.*, xxviii., 319). A freshly and properly prepared solution of hypobromite usually contains a little more than 50 per cent of bromide (see Note 1), but this increases more or less rapidly, and, ultimately, as the resultant of reactions (a) and (b), equals 83+ per cent. While the primary reaction of decomposition (b) is progressing, the secondary reaction of decomposition (c) adds a further small per cent of bromide (Bhaduri, *Zeit. Anorg. Chem.*, xiii., 385). Various solutions of "hypobromite" may therefore have their bromine distributed within the following limits:—



While engaged in other lines of research it became necessary to determine all of the halogen ions of such a mixture. On employing the methods of analysis then in use, it was found that they were either unreliable and inadequate or too laborious for our purposes. As the result of further investigation it was found that Volhard's method of titration, with modifications, could be employed for the rapid and accurate determination of all three components of such or any other homologous mixture of halogen acids.

Briefly considered the methods herewith given are based on:—(I.) The precipitation in alkaline solution of the bromide as $AgBr$; (II.) the decomposition of the hypobromite by means of ammonia,—



or hydrogen peroxide (*Journ. Am. Chem. Soc.*, xxix., 1316, $NaOBr + H_2O_2 \rightarrow O_2 + NaBr + H_2O$), and the precipitation in alkaline solution of the resulting total halide; (III.) the decomposition of the hypobromite with ammonia, the reduction of the bromate with iron and dilute sulphuric acid, and the titration in acid solution of the total bromine.

Analysis of Mixtures of Bromine Acids.

METHOD I. For Bromide.—A measured volume of the "hypobromite" solution in an Erlenmeyer flask is treated somewhat slowly with an excess of $N/10$ silver nitrate. During the addition of the latter, the mixture is shaken vigorously so that the formation of the silver bromide may be favoured, and the silver oxide, which is formed in alkaline solution after all of the bromide is precipitated, may be recognised by its dark brown or black colour. If the solution is not already sufficiently alkaline, more sodium hydroxide is added before the silver nitrate is run in, for, in the absence of sufficient alkali, all of the excess of silver nitrate will not be precipitated as silver oxide, and the completion of precipitation of the silver halide will not be definitely indicated. Next, sufficient dry acid sodium carbonate (see Note 2) is added to convert the sodium hydroxide into sodium carbonate and the silver oxide into silver carbonate, the colour of the precipitate thereby being changed from brown or black to white or light yellow.

The well-shaken precipitate is freed from the solution containing the oxygen halogen salts, by decanting, filtering,

and washing through a Gooch funnel (see Note 3), no effort being made to transfer the precipitate to the funnel. The filter flask is emptied and washed, the Gooch funnel is re-adjusted, the precipitate in both the flask and the funnel is treated with dilute nitric acid, and the excess of silver nitrate is filtered and washed into the filter flask, and titrated in the usual manner by the Volhard method. The difference between the N/10 silver nitrate and the N/10 potassium thiocyanate used is equal to the bromide in terms of N/10 silver nitrate.

METHOD II. For Hypobromite.—A measured volume of the solution in an Erlenmeyer flask is treated with a slight excess of ammonia or hydrogen peroxide to decompose the hypohalite (see Note 4). Boiling is necessary to discharge the excess of ammonia since it dissolves silver halide. With hydrogen peroxide no boiling is necessary. The solution is next treated with an excess of N/10 silver nitrate, acid sodium carbonate, &c., as in Method I. Filtering here may be made through an ordinary paper-filter instead of through a Gooch funnel. (Filtering is necessary to remove the bromate and other trioxxygen halides, since, when treated with nitric acid, they oxidise the thiocyanate used in the Volhard method). The difference between the N/10 silver nitrate and the N/10 potassium thiocyanate used is equal to the sum of the halide and the hypohalite, in terms of N/10 silver nitrate. The difference between the N/10 silver nitrate of this method and Method I. is equal to the hypohalite in terms of N/10 silver nitrate.

METHOD III. For Total Halogen and Bromate.—A measured volume of the solution in an Erlenmeyer flask is treated with sufficient hydrogen peroxide or ammonia to decompose the hypohalite. The solution is freely diluted with water, and then treated with a sufficient quantity of finely divided iron (Hendrixson, *Am. Chem. Journ.*, xxxii., 242; Tschernobeeff, *Chem. Ztg.*, xxix., 442; other reducing reagents have been employed with less success). While shaking vigorously, the solution is next acidulated with very dilute sulphuric acid. After corking the flask and letting stand for ten to sixty minutes, the solution is filtered and treated with an excess of N/10 silver nitrate. Nitric acid is next added, and the solution is boiled to oxidise the ferrous iron. After cooling, the excess of N/10 silver nitrate is determined with N/10 potassium thiocyanate, the iron already present being the indicator. The difference between the N/10 silver nitrate and the N/10 thiocyanate is equal to the total halogen present in terms of N/10 silver nitrate. The difference between the N/10 silver nitrate of this method and Method II. is equal to the bromate in terms of N/10 silver nitrate.

Analysis of Mixtures of Chlorine Acids.

Solutions of ions containing chlorine are analysed as above; bleaching powder involves certain modifications of weighing, of breaking up of the insoluble particles, of first adding sodium hydroxide, then acid sodium carbonate, &c., that are sufficiently obvious.

Analysis of Mixtures of Iodine Acids.

For the reason that silver iodate is insoluble in neutral solution but soluble in alkaline solution, whereas silver iodide is insoluble in both, a generous quantity of sodium hydroxide must be added in Method I. to keep the former in solution. The precipitate must be distinctly dark coloured and no acid sodium carbonate can be used. In Method II. sufficient ammonia is used to decompose the sodium hypiodate and keep the silver iodate in solution.

The advantages of these methods are (1) employment of volumetric solutions that are not only easily prepared but easily preserved; (2) the determination of the different halogen acids with the same volumetric solutions, thus eliminating errors and rendering the calculations easy; and (3) the methods are not only rapid but accurate.

In the following table, 1 grm. of bleaching powder (calculated), or 10 cc. of solutions were used in each analysis; the results are given in terms of N/10 AgNO₃ :—

Method.	Hypo-bromite solution.	Bromate solution.	Hypo-chlorite solution.	Bleaching powder.	Hypo-iodite solution.
I. . . .	76·74	62·04	12·77	78·43	100·30
I. . . .	76·72	62·12	12·68	78·49	100·42
II. . . .	138·44	62·15	23·79	92·57	101·45
II. . . .	138·30	62·04	23·65	92·51	101·43
III. . . .	142·34	73·28	24·02	96·90	121·36
III. . . .	142·27	73·20	24·01	96·96	121·25
N/10 Na ₃ AsO ₃	123·01	—	22·04	28·20	—
Calculated per cent of Total Halogen.					
HX	53·91	84·76	52·96	80·91	82·73
HOX	43·32	0·02	45·62	14·61	0·91
HXO ₃	2·77	15·22	1·42	4·48	16·36

It will be observed that the arsenite method of direct titration of hypohalous acids gives results in close agreement with the above methods. Though the three halogen ions of the above homologous mixtures may be estimated by combination of Method III. above, the arsenite method, and the iodometric method, three additional volumetric solutions are required, viz., N/10 sodium arsenite, N/10 sodium thiosulphate, and N/10 iodine and potassium iodide. For the reason that these solutions are unstable, the superiority of the above described methods is evident.

Notes.

1. Such a solution is best prepared by placing the NaOH solution in the lower part of an ordinary desiccator, the bromine in a dish in the upper part of the desiccator, and letting stand at ordinary or lowered temperature until the bromine has evaporated spontaneously. Such a solution contains nearly 50 per cent of its bromine as NaOBr, whereas solutions, prepared by adding bromine directly to alkali, usually contain less than 40 per cent of its bromine as NaOBr.

2. This acid sodium carbonate is necessary only in the case of chlorine mixtures; it may be omitted in the case of bromide mixtures, and must be omitted with iodine mixtures. It is necessary with chlorine for the reason that fixed alkalis but not alkali carbonates dissolve silver chloride. See also *Journ. Am. Chem. Soc.*, xxix., 269.

3. Filter-paper cannot be used unless approximate results only are desired, for the reason that hypohalous salts rapidly attack cellulose, and yield by decomposition the corresponding halide. The latter then reacts with the silver oxide present, and too high percentages of the halide in the sample analysed are indicated.

4. The hydrogen peroxide used must not precipitate with silver nitrate; if it does it should be treated with sufficient silver nitrate and filtered. When hydrogen peroxide is used the precipitate may remain dark coloured. —*Journal of the American Chemical Society*, xxxi., No. 5.

Double Sulphates of Calcium.—M. Barre.—The solubility of calcium sulphate is considerably increased by the presence of ammonium sulphate, and the double sulphate CaSO₄(NH₄)₂SO₄·H₂O is stable between 0° and 100° in presence of an excess of ammonium sulphate. A concentration of 35 per cent is necessary for the formation of this double sulphate. In presence of excess of calcium sulphate a second double salt is formed at 80°. This new double salt, which is decomposed by water like the first, may be obtained in the form of crystals when the transformation is effected in the neighbourhood of 80°. The formula of the new salt is 2CaSO₄(NH₄)₂SO₄. Calcium sulphate is less soluble in water containing potassium sulphate than in pure water. The double sulphate CaSO₄K₂SO₄·H₂O is stable from 0° to 99° both in presence of an excess of calcium sulphate and in presence of an excess of potassium sulphate. The double sulphate 2CaSO₄K₂SO₄·3H₂O, which Ditte stated he had obtained by the action of a cold concentrated solution of potassium sulphate on gypsum, is not formed in this interval of temperature. —*Comptes Rendus*, cxlviii., No. 24.

EXPERIMENTS AT HIGH TEMPERATURES AND PRESSURES.*

By RICHARD THRELFALL, M.A., F.R.S., Assoc.Inst.C.E., F.C.S.

WITHIN a few miles of this lecture room there is an unexplored region—to approach it we should have to move vertically downwards. It has been suggested by Mr.

direction, but the journey would be slow and the cost high—for instance, to bore a hole twelve miles deep was estimated to be a labour which would occupy eighty-five years and cost £5,000,000. A well-to-do man desiring to benefit his fellow creatures could not do better than undertake this project, but till he comes forward we must perforce be content to try to imitate in our laboratories the temperature and pressure conditions which would be met with deep down in the earth.

Information, attainable from experiments under these conditions, is essential to the development of any exact concept of the structure and evolution of the earth. One of the most important questions in connection with the study of bodies under high pressures and at various temperatures, is as to whether any particular body is solid or liquid under specified conditions, and, if solid, whether it is amorphous, glassy, or crystalline. That pressure would influence the melting-point of solids was clearly put forward by Clapeyron in 1834, but it was not till after the establishment of the mechanical theory of heat in the "forties" of the last century that the exact numerical relations could be established, as was done by Prof. James Thomson in 1851, when he calculated for the first time the amount by

which the temperature of fusion of ice would be reduced by a given increase of pressure. The ideas underlying such calculations are based on a consideration of the way in which heat is converted into mechanical work in any prime mover depending on a heat supply, and were first formulated by Carnot in 1824, before the true nature of heat was understood. As the matter is fully dealt with in every text-book, I will merely remind you that Prof. James Thomson was able to obtain an equation between the mechanical work actually produced under stated conditions and the work, which according to Carnot's principle, must be developed by a reversible engine operating between fixed temperature limits upon a given amount of heat.

The general relation for a substance undergoing a change of state at absolute temperature T , such change involving a change of volume Δv and an absorption or emission of heat at constant pressure Q_p , is, reserving the question of sign—

$$\frac{dT}{dp} = \frac{\Delta v T}{Q_p};$$

or in words, the change of melting-point produced by unit change of pressure, equals the product of the absolute temperature, and the ratio of the change of volume of unit mass on melting, to the quantity of heat absorbed or emitted by unit mass in the process.

Now the greater number of substances when they pass from the liquid to the solid state, evolve heat and contract in volume. An increase of volume is of course a positive quantity, and if heat is absorbed during this increase it is reckoned positive also. In the case of water, heat is evolved during freezing as in other cases, but the mixture of ice and water has a smaller volume than the solid ice. Accordingly the change of volume in this case is negative, and the melting-point falls as the pressure rises.

The first fairly exact confirmation of the theory appears to be due to De Visser (*Recueil des Travaux Chimiques des Pays-Bas*, 1893, xiii., 101), who selected acetic acid

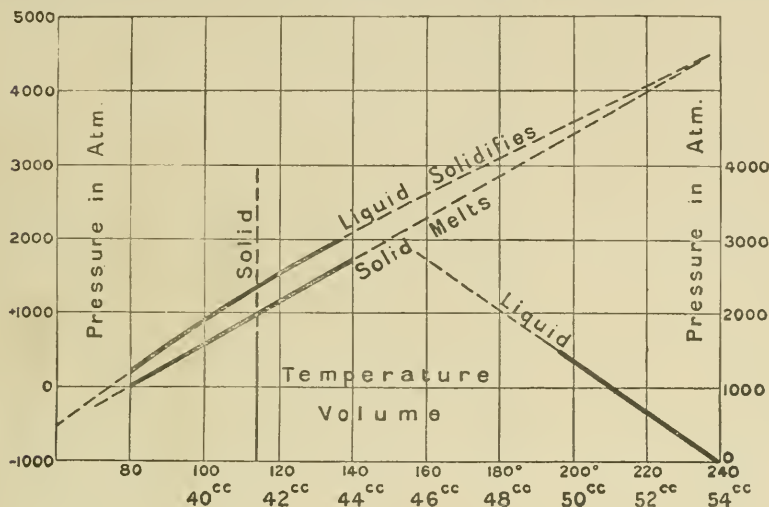


FIG. 1.—Full lines indicate party field actually explored. Dotted lines indicate extrapolations.

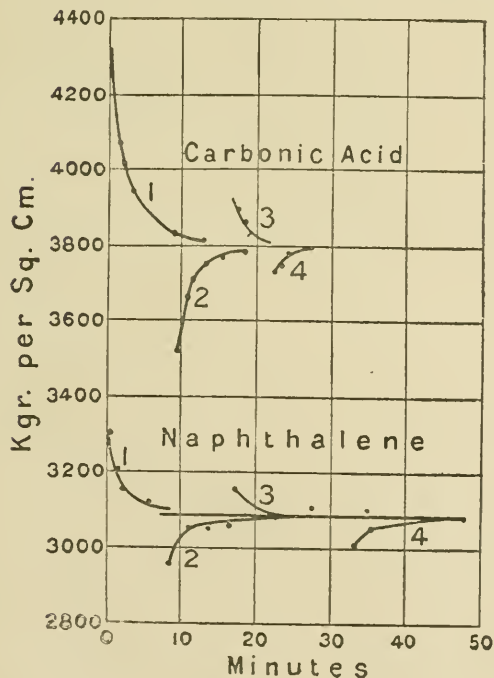


FIG. 2.

Parsons (*B.A. Reports*, Cambridge, 1904, 672) that it would be worth while to make a short expedition in this

*A Discourse delivered before the Royal Institution, March 19, 1909.

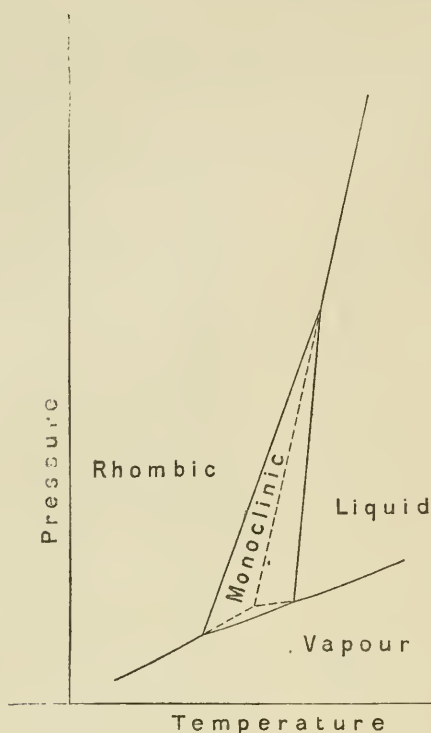


FIG. 3.

most carefully purified as a test substance—though valuable experiments up to much higher pressures had been previously made by many others—particularly by Dewar on water (*Proc. R. S.*, 1880, xxx., 533), Ferche on benzol (*Wied. Ann.*, 1891, xlv., 265), and Damien (*Comptes Rendus*, 1891, cxii., 785) on a variety of substances.

It is necessary to work with a pure substance in order to test the theory, or at all events with one whose solid phase has the same constitution as its liquid phase. If the acetic acid had not been pure the probability is that the frozen part would have contained more or less of the impurity than the unfrozen, and consequently a state of affairs not contemplated in the theory would have arisen. From the experimental point of view it is obvious that a sharp melting-point is a necessary condition for its accurate observation.

A quantity of acetic acid—rather over 40 cc.—is confined by mercury in a closed apparatus based on a previous design by Bunsen, which also contains air in a graduated tube. When the acetic acid melts, it expands and compresses the air through the intermediary of the mercury—whereby the pressure can be inferred. The part of the apparatus containing the acetic acid is immersed in a bath which can be kept at any desired temperature. As the melting progresses, a pressure is set up by the expansion, and finally attains such a value that no further melting can take place. We then have a mixture of solid and liquid acetic acid in presence of each other under a measured pressure and at a known temperature. The quantities entering into the calculation are ascertained from other experiments—notably the ratio of the change of volume to heat absorbed was ingeniously ascertained by a modification of Bunsen's ice calorimeter. The final result was that the rate of variation of temperature of melting-point with

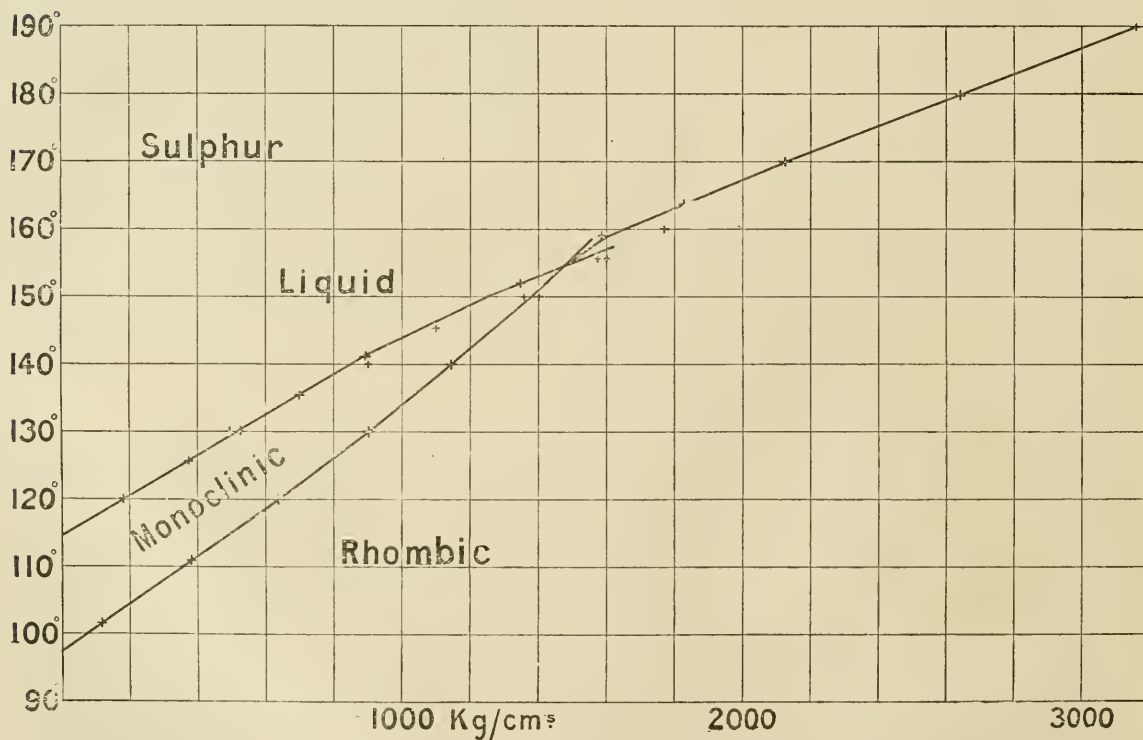


FIG. 4.

increasing pressure was calculated to be 0.02421° C. per atmosphere as against 0.02435° C. found by experiment—a difference of 0.57 per cent. I have dwelt on this work at some length in the hope that it may make the nature of the problem clear. It is to be noted that the experimental difficulties are considerable and are enhanced by the fact that we have no *a priori* reason to suppose that the rate of change of melting-point with pressure is a constant quantity independent of the pressure. In fact it was shown by Sir Joseph Thomson about 1886 ("Applications of Dynamics to Physics and Chemistry," 259) that in calculating the change of melting-point we ought to take into consideration "the difference between the energy due to strains produced by the pressure in unit mass before and after solidification." Sir Joseph Thomson's reasoning, based as it is on a generalised Lagrangian method of treating problems involving energy changes, is unsuited for discussion in a non-mathematical address, but it is easy to see that if the compressibilities of liquid and solid are different, then the change of volume accompanying the change of state of unit mass must itself depend on the pressure, and therefore the pressure change of melting-point which is proportional to the change of volume must depend on the square of the actual pressure so far as this part of the effect is concerned. This anticipation was realised by Damien in 1891, who showed that the melting-points of substances in terms of the pressure could be expressed by a formula of the kind—

$$t = t_0 + a(p - 1) - b(p - 1)^2$$

t_0 being m.p. under 1 atmosphere pressure.

I think we may add that there will also be a small effect depending on changes of energy in the capillary layer separating the phases.

The first adequate investigation of the change of m.p. under pressure over a wide range of pressures was made by Barus (*Bulletin* No. 96 U.S.A. Geological Survey, 1892). Time does not permit me to do more than exhibit the results obtained, though the apparatus employed was most cleverly designed. It requires great experimental knowledge and ingenuity to infer with accuracy changes of volume of a few per cent of the original volume at pressures of 1500 atmospheres, nearly 10 tons per square inch. If we note the pressures and temperatures of melting, and plot the result as a curve against the pressure and temperature, we obtain what is called a melting-point curve, and this divides the field into two parts, so that on one side of the curve the temperature and pressure at each point have such values that the substance is solid, while on the other side their values are such that the substance is liquid. It is instructive, therefore, to regard the melting-point curve as the line separating the region of solid from the region of liquid. Along the line, and along it only, *i.e.*, at the pressures and temperatures indicated by points on the line, the solid and liquid phases can exist in equilibrium together. Such a diagram is called a "Diagram of Condition" (Fig. 1).

By far the greater part of our information as to the quantitative relations of bodies at high pressures we owe to Prof. Gustave Tammann, who has collected his results in a book entitled "Kristallisieren und Schmelzen," whose advent (1903) must be regarded as an important event in the history of the subject.

The complete thermodynamic specification of a body

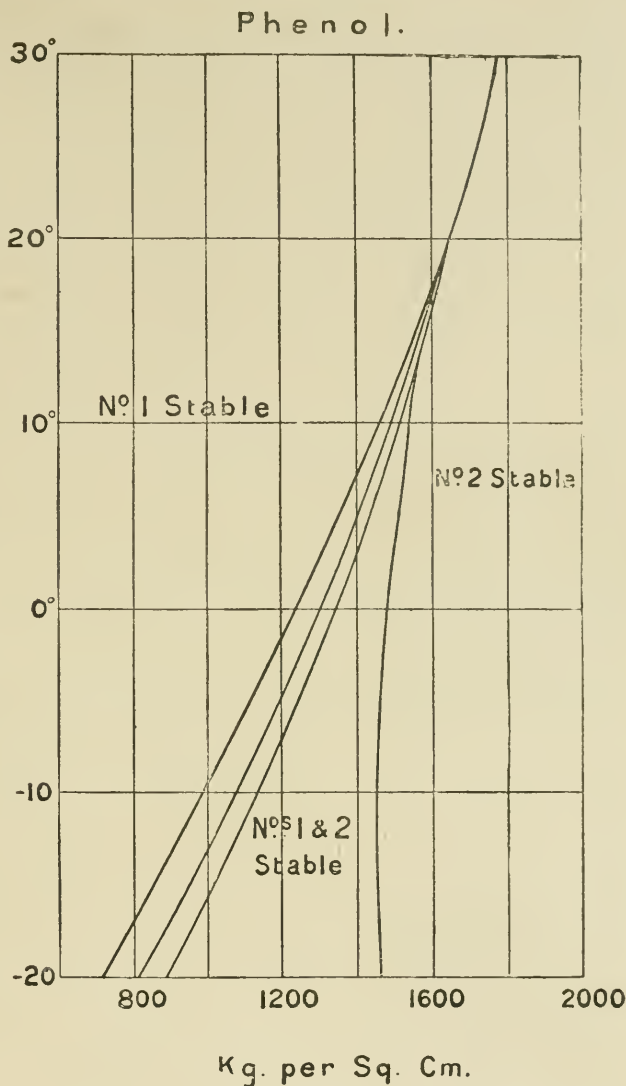


FIG. 5.

involves a knowledge of its mass, volume, pressure, temperature, energy, entropy, surface tension, and nature—whether liquid, solid, glassy, crystalline, or amorphous.

Prof. Tammann has simultaneously measured the pressure, temperature, volume, and mass of many substances under high pressure, and at temperatures extending from 80° to 200° C.—taking cognisance of the physical state—and has thus been able to plot out many interesting diagrams condition. The apparatus consists of a screw press by which a piston of ebonite is driven down a steel cylinder of small known cross-section. The cylinder is filled with oil, and the ebonite piston fits practically oil-tight. The oil communicates with the oil contained in a strong steel vessel which also encloses a glass tube open at the lower end, containing the substance and dipping below the level of mercury contained in a dish. The oil occupies the rest of the space. The steel vessel is placed in a thermostat so that its temperature can be ascertained. The oil pressure is measured by a Bourdon gauge which it was possible to

standardise, thanks to the previous work of Amagat and Tait. In order to construct a diagram of condition, it is necessary and sufficient to find a number of points separating the liquid from the solid area—or separating the areas corresponding to different crystalline forms in the case where the transformation of one sort of crystal into another is under investigation. To understand how this is done, it is best to take a special case. If we have a quantity of a substance under a known pressure and temperature in the piezometer and suddenly increase the pressure, so that there is not time for heat to pass in or out to any appreciable extent before the pressure gauge can be read, we have practically adiabatic compression. If the apparatus be then left to itself, the heat which we may suppose to be liberated by the pressure will slowly diffuse outwards, and the pressure will fall as time goes on. If we happen to start from a point on the melting-point curve before the pressure is raised—then the final result will be that we shall thaw or freeze more or less of the material, and the original pressure will be exactly regained, the change of state compensating the impressed change of volume. If, however, the increase of pressure has been so great that a change of state of the whole mass has been brought about, then the after variation of pressure will be so much greater that it is easy to distinguish this case from the previous one.

The accompanying diagram (Fig. 2) taken from Prof. Tammann's book shows how the equilibrium curve can be located in the case of carbon dioxide and naphthalene. In the former case the temperature was 31.3°C . The pressure was 3800 kilogrms. per sq. cm. or 24.13 tons per sq. inch. (157.49 kilogrms. per sq. cm. = 1 ton per sq. inch = 152.38 atmospheres).

The pressure was raised adiabatically to 4400 kg./cm.^2 (27.93 tons/sq. inch) and the subsequent fall of pressure plotted against a time scale for ten minutes. The pressure was then adiabatically reduced to 3550 kg./cm.^2 , and the recovery curve again plotted. The equilibrium pressure must lie between the pressures approached asymptotically on the diagram, i.e., between 3825 and 3792 kg./cm.^2 . A repetition between narrower pressure limits enables the pressure to be fixed at between 3808 and 3797 kg./cm.^2 . A similar procedure fixed the pressure of the melting-point of naphthalene between 3090 and 3080 kg./cm.^2 at the temperature considered—a difference which corresponds to 0.2°C ., the actual temperature possibly differing from the thermostat temperature by 0.1°C .

We may now pass on to the consideration of some of the results obtained, which refer not only to change of melting-points, but to changes in the temperatures of transformation of isomorphous forms.

As illustrations of such changes, I show here the transformation of yellow to red mercuric iodide, which shows well in the projection microscope; also Mitscherlich's transformation of potassium bichromate, and sulphur in two forms.

(Experimental Demonstration of a Transformation of Sulphur.)—A microscope slide is prepared by partially melting a fragment of monoclinic sulphur, and enclosing some of the melt between the slide and cover-slip, well pressed together. The presence of unmelted monoclinic sulphur insures the crystallisation of this variety on lowering the temperature. By means of a hot stage it is possible to preserve the crystallisation long enough to exhibit it by means of a projection polarising microscope. The appearance is very characteristic. Another slide is prepared, but this time all the sulphur is melted, and can generally be under-cooled so far that it crystallises in what is believed to be the octahedral system. This slide is then placed in the projection microscope, when it is seen that its appearance is totally different from that of the first slide. The preparation is then heated on the hot stage, and when the transformation temperature is reached it is seen that the structure begins to change—the crystallisation breaks up and becomes granular, the granules showing in general much more colour than the original crystallisation. These

granules are taken to be monoclinic sulphur. The temperature is now raised till about half the preparation has melted, and it is then allowed to cool back a little so as to crystallise. The crystals now show the characteristic monoclinic crystallisation with brilliant colours, since unmelted monoclinic sulphur is present).

The case of sulphur is one of great interest. It has long been known that sulphur can exist in at least three solid forms. It crystallises from some solvents in octahedral crystals, from others or from its liquid state in monoclinic crystals. In the latter case some amorphous sulphur is generally dissolved in the crystals, and the amorphous variety itself is formed in tough vitreous masses when molten sulphur heated till it becomes very viscous is poured into cold water. At ordinary temperatures the octahedral form alone is stable. It has been found that at atmospheric pressure octahedral sulphur is converted into monoclinic at 95.4°C ., and in the process 2.7 grm.-calories per grm. of sulphur are evolved. The density of octahedral sulphur is about 2.03 and of monoclinic about 1.98 at ordinary temperatures. In accordance with the principles developed previously the transformation temperature of rhombic to monoclinic sulphur must rise with increase of pressure. So far back as 1887 Roozeboom was able to predict that the diagram of condition for sulphur would be as shown at Fig. 3 (*Rev. Trav. Chim. Pays-Bas*, 1887, vi., 314).

Prof. Tammann has supplied the corroboration of the existence of the triple point.

Suppose that we have sulphur at a pressure of about 1500 kg./sq. cm. (9.52 tons/sq. inch) and raise its temperature to about 160°C . or more, we shall cut the melting-point curve of octahedral sulphur, and the sulphur will melt. If we then allow the sulphur to cool, keeping the pressure up, octahedral sulphur will crystallise from the melt instead of monoclinic sulphur. This very likely has some bearing on the occurrence of native crystals of octahedral sulphur (Fig. 4).

It is not every substance which has such sharply defined properties as sulphur, though even these are not as sharp as they might be, owing to the constant presence of amorphous sulphur. An instructive case is afforded by phenol. As the diagram shows (Fig. 5) there is a considerable region of the field in which two kinds of crystals of different density can exist together, the curves forming the boundary of this region of pseudo-equilibrium.

It may be that the two crystalline forms of carbon which apparently can exist together indefinitely at ordinary temperatures and pressures are an illustration of the same property.

As a final illustration we may note the results for water down to -80°C ., from which it appears that it possesses three allotropic crystalline forms with at least two melting-points.

The melting curves of from thirty to forty substances have been investigated, mainly by Tammann, up to about 3000 kg./sq. cm. = 19.05 tons/sq. inch, and the general result has been to show that there is a tendency for the rate of change of melting temperature with pressure to fall off as the temperature rises, and also that many substances, which at ordinary pressures crystallise in one form only, can be caused to assume allotropic modifications under high pressure. This tendency to form allotropic modifications appears to be associated with the extent to which a substance can be under-cooled without crystallising.

(To be continued)

β -Naphthane Diols.—Henri Leroux.—The author suggests the name naphthane for the decahydride of naphthalene. He has prepared and investigated the properties of the *cis* and *trans* β -diols, and has in addition obtained a third isomer produced by the combination of the two glycols, according to a reaction which appears to be common to many hydroaromatic compounds. The power of combining of the *cis* and *trans* glycols has only been observed when asymmetric carbons are present in the molecule of the diols.—*Comptes Rendus*, cxlviii., No. 24.

THE OXIDATION OF PHENOL.*

THE EFFECT OF SOME FORMS OF LIGHT AND OF ACTIVE OXYGEN UPON PHENOL AND ANISOLE.

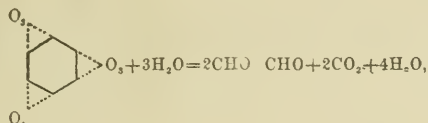
By H. D. GIBBS.

(Continued from p. 70).

The Action of Ozone upon Phenol.

OTTO observed that ozone reacts with phenol, producing a red colour (*Ann. Chim. Phys.*, 1898, [3], xiii., 136). He studied the reaction at 16° and 50°, and isolated no reaction products.

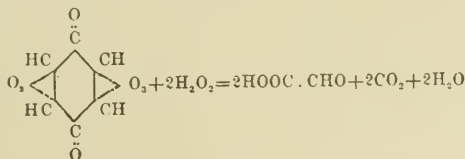
Dry ozone is, in general, not reactive. It is more reactive when traces of moisture are present (Richarz Uhrig, *Phys. Zeit.*, 1905, vi., 1). Pure dry ozonised oxygen will react at once with pure moisture free phenol in the liquid state, and more slowly when the phenol is in the form of crystals. The reactions which take place are largely influenced by the temperature. At the room temperature, 30°, the first action of the production of quinone, and possibly quinol, as indicated by the coloration. As the reaction proceeds an ozonide is undoubtedly produced. This is evidenced by the copious evolution of carbon dioxide and the formation of glyoxylic acid, a reaction analogous to the breaking down of the triozone of benzene, as demonstrated by Harries and Weiss (*Ber.*, 1904, xxxvii., 3431).



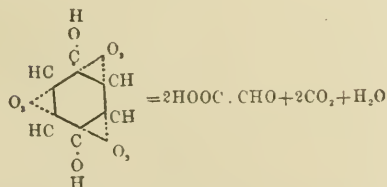
When ozone acts upon dry phenol, the water which seems to be necessary to the breaking down of the ozonide, and which also accelerates the reaction, is produced during the formation of quinone as follows:— $\text{C}_6\text{H}_5.\text{OH} + 2\text{O} = \text{C}_6\text{H}_4\text{O}_2 + \text{H}_2\text{O}$.

When ozone reacts upon moist phenol, the same reaction products are produced, quinol resulting in larger quantities than quinone.

Whether it is the diozonide of quinone or the triozone of quinol which breaks down according to the reactions—



or—



has not been determined. When dry ozone comes in contact with dry phenol, cooled in an ice-bath, the velocity of the reaction is very much reduced; the products, however, appear to be the same. Carbon dioxide is evolved, and no ozonide can be isolated. No attempts have been made to work at lower temperatures and employ solvents for the phenol, with the view of isolating an ozonide.

The Action of Nascent Oxygen, liberated at the Anode, upon Phenol.

By the action of the alternating current upon aqueous solutions of phenol in the presence of magnesium sulphate and magnesium hydrogen carbonate, Drechsel has obtained catechol, quinol, phenolsulphonic acid, γ -diphenol, formic acid, oxalic acid, succinic acid, and a number of other products (*Ann. f. Prakt. Chem.*, 1884, ii., pp. 29, 229; and 1888, ii., pp. 38, 67). The action of the alternating current in aqueous alkaline solutions has also been studied.

Bartoli and Papasogli have studied the products of the action of the direct current upon alkaline solutions of phenol (*Comptes Rendus*, 1882, xciv., 1339; *Gazz. Chim. Ital.*, 1884, xiv., 90).

It is to be expected that the oxidation of alkaline solutions of phenol will produce more complicated reaction products than when an acid solution is employed, for the reason that quinone is so easily oxidised to complicated products in presence of alkalis.

Experimental.

A concentrated aqueous solution of phenol, acidified with sulphuric acid to facilitate the passage of the electric current, was divided between two vessels connected by a syphon, and electrolysed with a direct current passing between platinum electrodes placed one in each vessel.

While the evolution of hydrogen was quite brisk from the cathode, very little oxygen escaped from the anode. The solution surrounding the anode quickly assumed a yellow colour deepening to a red, while that surrounding the cathode remained colourless. The anode became coated with a thick layer of a yellowish red substance, which was removed from time to time by washing the electrode in alcohol. This compound is insoluble in water, soluble in alcohol and in phenol, imparting to both solutions a brilliant red colour. It is in all probability one of the condensation products to which the coloration of phenol is to be attributed.

The solution around the anode was found to contain considerable quantities of quinone. No complete investigation of the reactions involved was attempted.

The Question of the Chemical Activity of Oxygen Gas Ions.

Experimental data seems to point to the fact that gas ions are not reactive in the chemical sense.

Gockel (*Phys. Zeit.*, 1903, iv., 602) found that the ionisation of ozonised oxygen made by passing oxygen over moist phosphorus was not destroyed by passing the gases through various solutions, water, potassium hydroxide, dilute and concentrated sulphuric acid, potassium permanganate, pyrogallol, potassium iodide, and oil of turpentine, even though the ozone was in some cases completely removed.

Bredig and Pemsler (Dammer, "Handbuch d. Anorg. Chem.," 1903, iv., 122; Eder, "Photochemie," Halle-a-S., 1906, 87; *Fahresb. d. Chem.*, 1899, i., 380) observed that the rate of the oxidation of sodium sulphite is not accelerated when the air, before passing into the solution, is exposed to the action of ultra-violet or Röntgen rays, uranium, or phosphorus. Ewan (CHEMICAL NEWS, 1894, lxx., 90) after studying the slow oxidation of phosphorus, sulphur, and acetaldehyde, concludes that in the process only a small portion of the oxygen which is dissociated into its atoms takes part in the oxidation. Van't Hoff (*Zeit. f. Phys. Chem.*, 1895, xvi., 411), in commenting upon the work of Ewan, says that the oxidation may be due to oxygen atoms or oxygen ions, and that it is not due to ozone. Eder ("Photochemie," Halle-a-S., 1906, 87) balances the evidence by saying that in the present state of our knowledge it is by no means concluded that oxidation is accelerated by contact of the oxidisable substance with the oxygen which has been ionised by exposure to light, and that ozone formation and ionisation are accompanying phenomena.

From the experiments performed with the apparatus shown in Fig. 1, it is to be concluded that another instance

* Contributions from Laboratory for the Investigations of Foods and Drugs, Bureau of Science, Manila, P.I. From the *Philippine Journal of Science*, vol. iv., No. 2.

has been added to those above cited, pointing to the inactivity of the oxygen ions in the process of oxidation. By means of this apparatus pure dry ozonised oxygen was brought into contact with pure dry phenol in the dark. The tube G, containing a length of 18 cm. of tightly packed glass-wool removed the gas ions (see Note) produced by the Brush discharge in the tube F, so that it is to be presumed that oxygen in the condition of O_2 and O_3 (and perhaps some atoms due to an equilibrium $O_2 \rightleftharpoons 2O$) only pass into the tube J containing the phenol. In some experiments the glass-wool filter was omitted from the chain and in others it was placed as shown in Fig. 1. In both cases the reaction with phenol in the liquid state, super-cooled or not, proceeded at once upon contact with the ozone, no ozone escaping reaction with the phenol, while with phenol which was entirely crystalline the reaction was very much diminished in speed. No variations were noted between the rate or character of the reaction due to the presence or absence of the ion filter in the apparatus chain.

While it is to be concluded from these experiments that ozone is a form of oxygen reactive with phenol, with or without the presence of the gas ions, it is not proved from the method of experimentation that the gas ions exert no influence.

(NOTE.—With respect to the removal of the ions formed by the action of Röntgen rays see Thomson and Rutherford, *Phil. Mag. and Journ. Sci.*, 1896, xlii., 392. With respect to ions formed in other ways see "Conduction of Electricity through Gases," 1906, II. On page 39 Thomson states:—"From these numbers we conclude that the ions produced by Röntgen rays, by radio-active substances, and by ultra-violet light are identical, a conclusion which we shall find confirmed by several other courses of reasoning.

Influence of the Glass of the containing Vessel on the Rate of Coloration.

Different varieties of glass have been found to show different absorption values to short wave lengths. Atmospheric air is more opaque to the most chemically active ultra-violet rays than fluorspar, rock salt, or quartz (Lenard, *Ann. der Phys.*, 1900, ccxvi., 486).

Phenol exposed to the action of the sun's rays is coloured more rapidly under quartz glass than under ordinary glass. A sample of pure phenol was divided into two equal portions in watch-glasses, one covered by a clear glass dish and the other by a quartz dish of almost exactly the same thickness, and placed side by side in the sun. The sample protected by the quartz glass distinctly showed more coloration in two hours. After several days the coloration of the two samples was found to have deepened in about the same ratio.

Two small thin glass bulbs of equal size inclosing equal quantities of phenol were placed in the sun, one protected by a soda-glass dish and one by a quartz dish. The coloration was noticeably more rapid under the quartz than under the soda-glass. Layers of equal thickness showed the difference in colour to be marked when viewed through a colour comparator.

The Production of Ozone in the Sunlight.

Atmospheric air and oxygen are ozonised by ultra-violet rays.

Lenard (*Ann. der Phys.*, 1900, lxx., 486) has shown that under their influence gases become conducting, and in the case of oxygen ozone is formed. These effects were brought about in air by the short wave lengths to which the atmosphere is comparatively opaque. Lenard's (*Phil. Mag.*, 1897, xliii., 254) observations that coal-gas or an atmosphere charged with coal-gas is even more opaque to the short wave lengths than pure air has been confirmed by J. J. Thomson (*Proc. Cambridge Phil. Soc.*, 1908, xiv., 419). Regner (*Ann. der Phys.*, 1906, cccxxv., 1033) has found the wave lengths below 200 μ to be ozone producing, while those above 257 μ have the opposite effect. Since Meyer (*Ann. der Phys.*, 1903, xii., 849) observed that the

ozone absorption spectrum shows a maximum at wave length 257 μ , it is to be expected that these waves will be most active in the process of deozoneisation. The oxygen absorption spectrum (Kreusler, *Ann. der Phys.*, 1901, vi., 418) begins about the wave length 193 μ and extends farther into the ultra-violet, and Lenard (*loc. cit.*) found that the region of greatest ozone production lies between the wave lengths 140 to 190 μ .

Since only the absorbed rays produce chemical re-activity it is evident that, as the character of the vibrations changes from the shorter to the longer wave lengths, the ozonisation process is changed to one of deozoneisation, the change in wave length producing this effect being about 60 μ ; that is, from 193 to 257 μ . The sun's rays being a mixture of wave lengths constantly changing in character as they pass through the earth's atmosphere, the shorter being absorbed, and, as suggested by Fisher and Braehmer (*Ber. der Deutschen Chem. Ges.*, 1905, xxxviii., 2639), with the formation of ozone, it is reasonable to suppose that the ozonisation process gradually changes to one of deozoneisation as the earth's surface is approached, and that greater quantities of ozone are not found near the surface, not so much through the destruction of ozone by oxidation, as Fisher and Braehmer have advanced, as through the influence of the longer wave lengths (see Note), the temperature also being an important factor. From the experiments of Regener it may be assumed that there is an equilibrium between O_2 and O_3 at every temperature, and that the concentrations of the molecular oxygen and the ozone depend, other conditions being equal, upon the concentrations or intensities of the various absorbed wave lengths in the rays to which the gas mixture is exposed. Moreover, Briner and Durand (*Comptes Rendus*, 1907, cxlv., 1272) have found that the temperature is an important factor in this equilibrium. Oxygen, under the influence of the silent discharge, reaches an equilibrium with 11 per cent ozone formation at -78° , while at -194° the conversion to ozone is practically quantitative.

(NOTE.—Ozone in the upper atmosphere will be swept to the surface by air currents. The variation in the amounts found in the surface atmosphere may be thus accounted for. Peyrou (*Comptes Rendus*, 1894, cxix., 1206) could find ozone in the atmosphere of Paris only when there were high winds. He, however, rather attributes the results to the circulation of ozone formed over growing crops. De Thierry (*Comptes Rendus*, 1897, cxxiv., 460) has observed that the quantity of ozone in the atmosphere increases with the altitude. At Chamonix, altitude of 1050 metres, the amount found was 3.5 mgrms., while at Grands-Mulets, Mont Blanc, altitude 3020 metres, 9.4 mgrms. per 100 cubic centimetres were found. Hartley (*Journ. Chem. Soc.*, London, 1881, xxxix., 127) states:—"The foregoing experiments and considerations have led me to the following conclusions: First, that ozone is a normal constituent of the higher atmosphere. Second, that it is in higher proportion there than near the earth's surface).

Elster and Geitel found that amalgams of sodium or potassium inclosed in glass vessels loose a negative charge in the daylight. J. J. Thomson ("Conduction of Electricity through Gases," Cambridge University Press, 1906, ccli.), referring to their work, stated that "The glass vessel would stop any small quantity of ultra-violet light which might be left in the light after its passage through the atmosphere." In this reference he must have had in mind the shorter wave lengths, for it can not be doubted but that wave lengths shorter than 300 μ reach the surface of the earth. Edmond Becquerel (*Ann. Chim. Phys.*, 1843, III., ix., 298), sixty-six years ago, with a crude apparatus and a flint-glass prism, succeeded in photographing the sun's spectrum to about the wave length 328 μ . Photographs made with improved apparatus show the Fraunhofer line U which has the wave length 294.8 μ . Since the limit of visual sensibility of the human eye is about 400 μ (Nutting, *Bull. Bureau of Standards*, 1908, v., 265, says 330 μ) the above statement of Thomson can not be considered as being strictly accurate.

It is evident that ultra-violet light will penetrate to the interior of a glass vessel exposed to the sun's rays, the quality of the glass being an important factor. Regener (*loc. cit.*) states that glass absorbs the ultra-violet rays below the wave length 300μ . Fisher and Braehmer (*loc. cit.*) have observed that the coloration of manganese glass is produced slowly in the sunlight, more rapidly in high altitudes than in the lowlands, and in a few hours on exposure to the rays of the quartz-mercury lamp, and further that this effect is due in the latter case neither to the cathode nor Röntgen ray, but to the ultra-violet light (Fischer, *Ber.*, 1905, xxxviii., 946).

From these considerations one would expect that, under the most favourable conditions, the production of ozone in the atmosphere at sea level would be at a minimum (in the absence of other catalysts than sunlight), while if the atmosphere or oxygen were inclosed in a glass vessel, possibly only traces or none whatever would be produced as a result of the action of the sun's rays, and that if an equilibrium between ozone and molecular oxygen is established it will lie at the point where the ozone concentration is extremely minute. (Ewell, *Electrochem. and Met. Ind.*, 1909, vii., 23) states that the equilibrium between oxygen and ozone at ordinary temperatures is almost infinitesimal).

While it is possible that ozone may be produced by radio-activity, since radio-activity is present in the atmosphere, and M. and Mme. Curie (*Comptes Rendus*, 1899, cxxix., 823) have found that radio-active barium produces ozone in the air, and Richarzy and Schenk (*Fourn. Chem. Soc.*, London, 1904, Abs. ii., 399; *Sitzungsber. Akad. der Weiss.*, Berlin, 1904, xiii., 490) have shown that oxygen is ozonised with feebly radio-active radium bromide, it does not seem probable than an equilibrium between the two oxygen states will be seriously affected by this influence, or that it requires serious consideration among the causes which produce the oxidation of phenol.

(To be continued).

THE ELECTROLYTIC PRODUCTION OF WHITE LEAD.*

By JNO. A. YUNCK.

IN considering so important a commercial product as white lead, one asks:—Is it possible to produce it electrolytically at a price and of a quality to compete with other existing methods? To make it useful to the arts and commerce it must stand on equal footing with the purely chemical product. That which has been done to the present day was largely experimental, though very much has been tried and various methods improved, but it has not been applied commercially, to my knowledge.

The writer has experimented for some years, and operated a small plant making about 50 pounds of white lead each day, for several months. The actual time consumed each day for corrosion was about five hours. In the course of our experiments, we tried a great many forms and variety of shapes of electrodes, both anodes and cathodes, also large number of solutions, of varying densities, and at various temperatures, as well as of physical conditions. Another important factor considered was the current densities, or ampères per square foot of anode surface; still another was to have the cathodes of about the same resistance as the anodes, and keeping the condition of the electrolyte at as near a uniform temperature as possible.

By this way we were enabled to produce white lead equal to the best for covering and colour qualities. The experiments referred to were conducted at the laboratories of the late Rev. John B. Tibbits, at Hoosick, N.Y. The apparatus consisted of a tank about 36 inches high, by 24 wide, and 30 inches long (with glass sides to note the

operation). On the top of the tank were suitably arranged copper conductors to which the anodes of lead and cathodes of aluminium were fastened. At first we used solid lead plates about $\frac{1}{4}$ inch thick, 24 inches long, and 12 inches wide, and cathodes nearly the same dimensions. The distance between the plates was about $\frac{1}{2}$ inch; this worked very well for a time, but owing to improper circulation of the electrolyte local action soon set in and heated the solution so that the production slackened, and we found it necessary to stop to cool off the solution.

We arranged the tank so as to have running water surrounding it to keep it cool, and at the same time placed in the bottom of the tank a device which kept the solution in a slow steady motion. We cast the anodes and cathodes in strips or grids connected at top and bottom. After that we were enabled to continue the operation continuously. We used for an electrolyte two solutions, one of a 15 per cent solution of nitrate of soda, the other of nitrate of ammonium. The first was cheapest in first cost, though in the opinion of the writer ammonium nitrate being a better conductor, it would be cheaper from a commercial standpoint to use it. During the corrosion carbon dioxide gas was allowed to pass through the electrolyte from small orifices at the lower part of the tank. After running for about two hours and a-half, we stopped the operation for about half-an-hour to allow thorough settling, the solution was drawn off, and the precipitated white lead was removed, washed, and dried. The current used was 10 ampères per square foot anode surface, and from 1 to 2 volts.

As the electrolytic solution is made up of sodium and ammonium nitrate in water, and the solution is saturated with free carbon dioxide, the reaction taking place upon passage of the current can be described as follows:—The solution is decomposed, yielding at the anode nitrogen pentoxide, ozone, and oxygen, and at the cathode, sodium hydrate, ammonium, and hydrogen. The lead is attacked by the powerfully oxidising nitrogen pentoxide, N_2O_5 , and ozone; since nitrogen pentoxide in the presence of water is decomposed and forms nitric acid, HNO_3 .

During the double decomposition which takes place, nitric acid, HNO_3 , and hydroxide of lead, $Pb(OH)_2$, are formed. The nitric acid combines with the free ammonia and sodium hydrate to again form sodium nitrate, while the plumbic hydrate is precipitated by the free carbon dioxide present and forms finally the hydrated carbonate of lead, $2PbCO_3 + Pb(OH)_2$. Thus it is seen that, although the solution is decomposed by electrolysis, it is regenerated by the chemical reactions taking place, and the only materials consumed are some lead, carbon dioxide, and water.

By this process we produced a white lead that was finer than can be ground by any mechanical means, and the finer the particles the greater the covering properties. The best commercial white lead contains the greatest amount of water, the amount running up to 2 per cent. This quality is more or less difficult to obtain ordinarily, but in the electrolytic process it is very easy; furthermore, this process produces the lead in a very finely divided state. There is no way at the present time open or known to the chemist by which white lead can be made or produced without free carbon dioxide.

One hundred pounds white lead is composed of about 80 pounds metallic lead, 12 pounds carbon dioxide, 2 water, and 6 oxygen, forming an oxy-carbonate of lead. Pure carbonate of lead is unfit for painting purposes; the combination with the oxide and water renders it much more opaque, and therefore of greater covering qualities.

Now comes the question from a commercial standpoint: Can we produce this product at a profit to the manufacturer? This can be answered, yes.

The current cost for a ton of white lead would be about 16 kilowatt hours; the cost of such materials as nitrate of sodium or ammonium could be counted as a fixture, because they are regenerated with only the slight loss that is due to the washing of the precipitate. The only loss is the water and a small amount of the carbon dioxide. The installation of a plant costs very much less than old methods,

* A Paper read at the Fifteenth General Meeting of the American Electrochemical Society, at Niagara Falls, Canada, May 6 to 8, 1909.

which involve the enormous outlay of the old corroding process, where capital is idle for months, not earning anything. The electrolytic method can convert metal into the carbonate from day to day. The health of the operators should also be taken into consideration; as this method can be worked so automatically that the human hand need not come in contact with the product, as most of this operation is conducted under water. I have worked still another process, somewhat similar to the one described, with exception that the carbon dioxide is generated simultaneously with the precipitation. The writer will make this the subject of another paper.

As to the production of colours, where the anodes are composed of bimetallic substances, lead in combination with copper, nickel, or iron, and whereby various colours and shades are produced, this is a large subject with which I am unable to deal fully this time, but will do so in the near future. Colours of the most delicate shades and tints can be produced, of different kinds, with ease. The precipitation being uniform when different electrodes and electrolytes are used, iron oxide paints of particular richness in texture as well as colour are produced this way, and very cheaply. The writer has on exhibition some specimens made some years ago of both white lead and colours.

NOTICES OF BOOKS.

The Manufacture of Rubber Goods. By ADOLF HEIL and Dr. W. ESCH. English Edition by EDWARD W. LEWIS, A.C.G.I., F.C.S. London: Charles Griffin and Co., Ltd. 1909.

THE principles applying to the manufacture of all classes of rubber goods are fully discussed in this book, which deals only with the use of rubber after it has left the plantation. Methods of vulcanising, both by the older and the so-called "cold" process, are described, the details relating to machinery and manufacture being slightly altered from the original in cases in which the practice in this country differs from that of Germany. The manufacture of all classes of rubber goods is treated in full, and the making of ebonite and ebonite articles is also included. The treatment of rubber waste, both in the rubber factory and in works built specially for the purpose, is discussed in an appendix. The book is a useful handbook for chemists and manufacturers employed in the rubber industry, and can lay claim to completeness of treatment, while it is in addition thoroughly practical and clear.

The Rise and Progress of the British Explosives Industry. London and New York: Whittaker and Co. 1909.

THIS book, which is published under the auspices of the Seventh International Congress of Applied Chemistry by its Explosives Section, is composed of articles which are chiefly historical on the explosives manufactured in this country. The first part contains an account of the preparation of all kinds of explosives from the earliest times, the chronology going back to Roger Bacon's prescription for making gunpowder. In the second part descriptions are given of the various factories in which explosives are made, both government and private establishments being included. The book is embellished with many reproductions of photographs of men whose names have been made famous by their work on explosives, and with illustrations of works which are typical or are of special historical interest.

A Manual of Volumetric Analysis. By HENRY W. SCHIMPF, Ph.G., M.D. Fifth Edition. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1909.

THE volumetric methods of analysis which are applicable for the testing of foods and drugs are very fully treated in

this book, the fifth edition of which has been considerably enlarged. The general principles of volumetric analysis are carefully explained, many examples being given of the methods of making the necessary calculations. The treatment of indicators of all classes is very full, and the latest improvements and adaptations of measuring vessels and other apparatus are included. The experimental directions are in all cases minute and detailed, and no volumetric method which is reliable and useful is passed over. The analysis of waters, sugars, and organic medicinal substances is described in the last part of the book, and a short account is given of some gasometric methods. The work will be found valuable as a reference book for students' use and also for practising analytical chemists.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlviii., No. 25, June 21, 1909.

Dimethylcamphor and Dimethylcampholic Acid.—A. Haller and Ed. Bauer. —The two atoms of hydrogen of the CH_2 group near the carbonyl group CO in camphor can be replaced by two alcoholic radicles, and the dimethylcamphor which is thus obtained can be transformed into the amide of dimethylcampholic acid when its solution in benzene is heated with sodamide. Only the monoalcoholic derivatives can be made to yield oximes by combining with hydroxylamine.

Heat of Polonium.—William Duane. —The author has found that the heat generated by a salt of polonium amounts to 0.0117 cal. per hour. The ionisation produced by a polonium salt can be compared with that produced by a known amount of radium under the same conditions, and when this is done it is found that polonium and radium in quantities which give the same ionisation currents set free almost the same amounts of heat. This agrees with the hypothesis that the heat disengaged by these substances is due to the kinetic energy of the α -rays.

Action of some Organomagnesium Compounds on 2-Methyl-4-pentanone.—F. Bodroux and F. Taboury. —The action of organomagnesium compounds on 2-methyl-4-pentanone gives (1) the ethylene hydrocarbon corresponding to the tertiary alcohol which would normally be formed; (2) a variable yield of the tertiary alcohol (40 to 60 per cent); (3) higher compounds of indefinite boiling-point in small quantities. Except in the case of phenylmagnesium bromide the ethylene hydrocarbon formed cannot be isolated in the pure state, as its boiling-point differs but little from that of the methyl pentanone.

Derivatives of Thioindigo.—M. Béchamp. —Thioindigo reacts energetically with organomagnesium compounds, but when water is added a white product is formed which turns red rapidly and regenerates thioindigo. When chloride of acetyl or benzoyl is added to the product stable compounds are obtained, but whatever the magnesium compound used the acetyl and benzoyl derivatives are identical. Hence it seemed probable that the organomagnesium compound acts merely as a reducing agent, and this hypothesis is verified by the fact that when thioindigo is reduced by tin and hydrochloric acid and then acetylated or benzoylated the same derivatives are obtained.

Elateric Acid.—A. Berg. —Elateric acid can be obtained by the action of potash or soda upon elaterine. Acetic acid and elateridine are first formed, and the latter is transformed into elateric acid. The formula of the acid is $\text{C}_{23}\text{H}_{38}\text{O}_7$, and all its salts are amorphous.

THE CHEMICAL NEWS.

VOL C., No. 2595.

THE BROMATES OF THE RARE EARTHS.

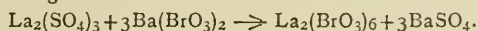
PART II.—THE BROMATES OF THE CERIUM GROUP AND YTTRIUM.

By C. JAMES and W. F. LANGELIER.

On page 182, vol. xxx., of the *Journal of the American Chemical Society* a new method for the separation of the yttrium earths was described, which involved the fractional crystallisation of the bromates (see also *CHEMICAL NEWS*, 1908, vol. xcvi., p. 61). As this method gave—and is still giving—excellent results, it was decided to investigate the pure bromates of all the rare earths. This paper describes the preparation and properties of the bromates of lanthanum, cerium, praseodymium, neodymium, samarium, and yttrium. Though some of these compounds have been prepared by the early investigators, it is doubtful if their material was very pure.

The bromates are usually prepared either by dissolving the oxide of the element in bromic acid, or by the metathesis of the sulphate of the metal with barium bromate. In the former case there is nearly always an excess of bromic acid which causes trouble during the subsequent evaporation. The latter method is preferable, since barium bromate is soluble in about 130 parts of cold water, and its solubility decreases enormously in the presence of the very soluble bromates. Thus we can employ an excess of barium bromate, and very readily obtain pure bromates by crystallisation. Because the rare earth sulphate solutions deposit crystals upon heating, it is best to cover the barium bromate with water, heat upon the water-bath, and add gradually, with plenty of stirring, the sulphate of the desired element. Under these conditions one encounters no difficulties, and the barium sulphate filters well.

Lanthanum Bromate, $\text{La}_2(\text{BrO}_3)_6 \cdot 18\text{H}_2\text{O}$.—This salt was prepared by the double decomposition of lanthanum sulphate solution upon barium bromate, according to the following reaction:—



The product of the reaction was filtered, the filtrate boiled down, and allowed to stand, when the remainder of the barium bromate separated. The re-filtered liquid was further concentrated, and the lanthanum bromate crystallised out. The crystals were then drained upon a Hirsch funnel at the filter pump, and, lastly, dried in the air upon filter-paper. When found necessary this material was re-crystallised.

Lanthanum bromate forms colourless hexagonal prisms. However, it usually separates out in small crystals about the size of granulated sugar. When the dried salt is ground up it apparently tends to give up a small part of its water of crystallisation, which causes the resulting powder to cake together. If alcohol is added to a saturated solution of this compound two layers are formed, the lower of which crystallises with difficulty upon continued stirring. The essential characteristic of this bromate is its great solubility in water as compared with the other bromates of the cerium group. One hundred parts of water dissolve 416 parts of the salt at 25° C. This does not agree with the results obtained by Marignac, who according to Urbain (Moissan, "Traité de Chimie Minérale," iii., 842) and other authors, gives the solubility as one in three and a-half parts of water at 15° C. The solubility does not differ anything like that extent between these two points. Lanthanum bromate varies from the most soluble yttrium earths with regard to the respective solubilities in alcohol,

as "ytterbium" bromate is soluble, while lanthanum bromate is insoluble. The bromate of lanthanum has a very great tendency to form supersaturated solutions. The melting-point of this substance in its own water of crystallisation is about 37.5° C., which is very low when compared with the other members of the group.

Analysis.	Theoretical.	Found.
Br_2O_5	52.53	52.83
La_2O_3	23.80	23.95
H_2O (difference) ..	23.67	23.22

When $\text{La}_2(\text{BrO}_3)_6 \cdot 18\text{H}_2\text{O}$ is heated for some time at 100° it loses water, forming a lower hydrate corresponding to the formula $\text{La}_2(\text{BrO}_3)_6 \cdot 4\text{H}_2\text{O}$.

	Theoretical.	Found.
Loss of water ..	18.41	18.57

The anhydrous salt was obtained by heating the lower hydrate to 150°. On heating to a high temperature it decomposes, giving out light and heat.

Cerous Bromate, $\text{Ce}_2(\text{BrO}_3)_6 \cdot 18\text{H}_2\text{O}$.—The preparation of this compound presents greater difficulties owing to the fact that the salt decomposes readily when heated in aqueous solution. Finally, the evaporation was carried out in a vacuum at about 35° C. The concentrated solution obtained in this manner was allowed to crystallise. These crystals were dried entirely by suction, because the mother-liquor contains another compound more highly oxidised, which causes filter-paper to ignite explosively.

Cerous bromate forms colourless hexagonal crystals. After keeping, the crystals become slightly coloured and an odour of bromine develops. Its most important property is its tendency to decompose, forming an insoluble basic compound, while some cerium is left in solution, probably in the state of ceric bromate. Cerous bromate melts at 49°, and decomposes just above this temperature. It is very soluble in water, coming between lanthanum and praseodymium bromates, but the rapidity of its decomposition prevented its accurate determination.

Analysis.	Theoretical.	Found.
Br_2O_5	52.43	52.68
Ce_2O_3	23.95	23.93
H_2O (difference) ..	23.62	23.39

Ceric Bromate, $\text{Ce}(\text{BrO}_3)_4$.—This compound is probably the powerful oxidising substance left in solution through the partial decomposition of cerous bromate. An attempt to prepare this ceric compound was made by dissolving hydrated cerium dioxide in bromic acid, and evaporating in a vacuum at 35°. A reddish brown liquid was obtained which required very careful handling, as it causes explosive combustion of organic material. Unfortunately, owing to an accident, the solution was lost before it could be definitely proved whether or not it was possible to isolate it in the crystalline form. This subject will be taken up again at the earliest opportunity.

Praseodymium Bromate, $\text{Pr}_2(\text{BrO}_3)_6 \cdot 18\text{H}_2\text{O}$.—This bromate, obtained in a similar manner to the lanthanum compound, forms green hexagonal prisms isomorphous with the other rare earths. Its melting-point is about 50.5°. One hundred parts of water dissolve 190 parts of the solid at 25°.

Analysis.—The Pr_2O_3 was estimated by titrating the oxalate with potassium permanganate.

	Theoretical.	Found.
Br_2O_5	52.42	52.55
Pr_2O_3	23.97	24.00
H_2O (difference) ..	23.61	23.45

On heating the normal hydrated bromate for some time to 100° it lost water, forming $\text{Pr}_2(\text{BrO}_3)_6 \cdot 4\text{H}_2\text{O}$.

	Theoretical.	Found.
Loss of water ..	18.37	18.29

The anhydrous salt was decomposed with evolution of heat and light by heating to 150° , while it can exist at 130° .

Neodymium Bromate, $\text{Nd}_2(\text{BrO}_3)_6 \cdot 18\text{H}_2\text{O}$.—This salt crystallises in hexagonal prisms possessing the colour characteristic of neodymium compounds. It melts about 66.7° . With regard to its solubility it lies between praseodymium and samarium bromates. One hundred parts of water dissolve 146 parts $\text{Nd}_2(\text{BrO}_3)_6 \cdot 18\text{H}_2\text{O}$ at 25° . Like the corresponding salts of lanthanum and praseodymium it does not dissolve in alcohol.

Analysis.	Theoretical.	Found.
Br_2O_5	52.12	52.19
Nd_2O_3	24.39	24.34
H_2O (difference) ..	23.49	23.47

When heated to 100° the normal salt loses water readily, forming $\text{Nd}_2(\text{BrO}_3)_6 \cdot 4\text{H}_2\text{O}$.

	Theoretical.	Found.
Loss of water ..	18.27	18.29

The anhydrous salt was obtained by heating to 150° , and decomposes with evolution of light and heat on heating to a higher temperature, but less violently than any of the preceding.

Samarium Bromate, $\text{Sm}_2(\text{BrO}_3)_6 \cdot 18\text{H}_2\text{O}$.—This compound, prepared according to the method already described under lanthanum, forms yellow coloured crystals of the same system as those previously mentioned. It melts at 75° and is the least soluble of the cerium group bromates, for 100 parts of water dissolve only 114 parts of the salt at 25° . This substance is very slightly soluble in alcohol.

Analysis.	Theoretical.	Found.
Br_2O_5	51.69	51.66
Sm_2O_3	25.04	24.97
H_2O (difference) ..	23.28	23.37

When the salt containing 18 molecules of water of crystallisation is heated to 100° it becomes constant after a long time. The resulting hydrate corresponds to 4 molecules of water similarly to the other members of the group.

	Theoretical.	Found.
Loss of water ..	18.11	18.34

All water of crystallisation is lost at 150° , while the salt decomposes at a higher temperature.

Efforts were made to utilise the fact that cerium bromate readily undergoes decomposition in aqueous solution to purify this element, and as a means for its gravimetric estimation. Experiments along the latter direction, in which many mixtures were tried, showed that a complete separation was impossible. The mixed bromates were dissolved in water, evaporated to dryness, placed in a steam-oven for an hour, and the residue taken up with water. Upon filtering off the insoluble portion, washing, and igniting, it was found that only 90 per cent of the cerium had been separated. The filtrate was again boiled down to dryness, and treated as in the first case. About 7 per cent more was obtained by this second operation. The third operation gave usually about 1 to $\frac{1}{2}$ per cent. On the other hand, this principle can be employed for the purification of cerium. By heating a mixture of cerium bromate with an excess of "didymium" bromate, cerium material was obtained in the first operation, which did not show any absorption bands even when observed through a thick layer of the concentrated solution. The second precipitate above mentioned is found to contain some didymium when the spectroscope is brought to bear upon the solution.

The fact that neodymium bromate is less soluble than praseodymium bromate is well worthy of being especially emphasised, as it gives a method in which the former is obtained in the least soluble portion. This separation proved to be much better than one would suspect after testing the solubilities. After three series of crystallisations of didymium, free from lanthanum and samarium,

the end fractions showed different colours. After six series the most soluble took on a greenish tint. By the time the tenth series were reached the most soluble was green, although it still showed faint neodymium bands. The least soluble showed the raspberry tint due to neodymium. By spontaneous evaporation we can obtain pinkish crystals, while the mother-liquor dries up around them, forming a deep green crust. As lanthanum bromate is very soluble and tends to form supersaturated solutions readily, one would expect to find this a very good method for its purification. This was not tried, as the conversion to the bromate takes some time when working with large quantities of material. Also, it is doubtful if it could compete with the simple method of the double ammonium nitrates. The bromates of Nd and Pr crystallise nicely even when small portions are worked.

Yttrium Bromate, $\text{Y}_2(\text{BrO}_3)_6 \cdot 18\text{H}_2\text{O}$.—The material used in the preparation of this compound was purified by a modification of the Muthmann and Böhm chromate process; the essential difference being that in the modified method the oxides are dissolved in nitric acid, after which potassium dichromate is added and the whole fractionated by means of a solution of potassium chromate according to the original method. This method is much more economical, and appears to give results which are just about as good.

The bromate was prepared by the double decomposition between yttrium sulphate and barium bromate.

It forms colourless hexagonal prisms isomorphous with the other bromates. One hundred parts of water dissolve 168 parts of the solid. This brings the solubility between the bromates of praseodymium and neodymium. It is slightly soluble in alcohol.

Yttrium bromate melts at 74° . If it is heated still further, some of the lower hydrate separates out. It was thought that this might be used for separating yttrium from erbium. It was found, however, that when a mixture of yttrium and erbium bromates was treated in this way and filtered, keeping the temperature constant, yttrium carried erbium along with it.

Analysis.	Theoretical.	Found.
Br_2O_5	56.66	56.74
Y_2O_3	17.80	17.85
H_2O (difference) ..	25.54	25.41

The normal hydrate was then heated for some time at 100° , when it lost water, being converted into a hydrate containing 6 molecules of water of crystallisation; hence, we find a difference from the cerium group, as they contain 4 molecules of water in the lower state of hydration.

	Theoretical.	Found.
Loss of water ..	17.02	17.26

Summary of the Cerium Group.

	La.	Ce.	Pr.	Nd.	Sm.
Melting-points	37.5	49	56.5	66.7	75
100 parts H_2O dissolve ..	416	—	190	146	114

The lower hydrates containing 4 molecules of water of crystallisation are obtained by heating the normal hydrates to 100° .

The anhydrous salts are obtained by heating to 150° with the exception of praseodymium, which should not be heated above 130° .

The property possessed by cerium bromate to decompose can be used for purifying this element.

Because the praseodymium salt is more soluble than that of neodymium the latter can be obtained in the least soluble portion, and in this respect differs from nearly all the other methods for its separation.

In conclusion it may be as well to mention that the third part of this paper will appear shortly. We also acknowledge our indebtedness to the Welsbach Company for material supplied for further investigation through the courtesy of Dr. H. S. Miner.

New Hampshire College, Durham, N.H.,
June 9, 1909.

EXPERIMENTS AT HIGH TEMPERATURES AND PRESSURES.*

By RICHARD THRELFALL, M.A., F.R.S., Assoc.Inst.C.E., F.C.S.

(Concluded from p. 80).

A QUESTION of the greatest interest and importance may now be formulated—What will happen if we go on increasing the pressure? Will a state of affairs be reached in which it is no longer possible to distinguish between the liquid and its crystalline form? Will there be, in fact, a sort of critical-point at which the melting curve will end? At present we can only say that no indication of such an occurrence has been observed experimentally, and Prof. Tammann takes the point that it is highly improbable that anything in the nature of continuous transformation can take place, because a crystal has different properties in different directions related to its axes, and there is thus a much greater qualitative difference between crystals and liquids, than between liquids and gases, both of which are isotropic. I must admit that this argument does not appeal to me very strongly. If it be possible to compress a substance till it reaches a state in which, at one and the same temperature, the liquid has the same density as the crystals, presumably the mean distance of the molecules will be the same in both cases. I see nothing monstrous in the view that under these circumstances crystallisation may set in gradually, and that it may not be possible to say exactly when the liquid ceases to be a fluid and becomes a crystalline solid. There are no theoretical or other grounds for supposing that the phenomena of crystal growth as observed when there is a change of volume accompanying the crystal formation, will necessarily hold when no such change of volume occurs.

If we refer to the theory of the change of melting-point by pressure it is obvious that if either the change of volume or the latent heat of melting vanish at any temperature or pressure on the melting curve, then in the neighbourhood of this pressure the curve must degenerate to a point—or small pressure changes will not affect the melting-point. It was pointed out, however, that there is a term or terms depending on the square of the pressure, and if these were relatively important the only thing we should notice would be a change of curvature at the point under consideration. It does not follow that there is no maximum or minimum to the melting temperature of any particular substance because the term in P^2 may be vanishingly small; it may be (and generally is) of opposite sign to the term in P , and in this case it is only a question of the relative importance of the terms where the maximum or minimum melting-point lies. Damien's empirical formula expresses precisely the effect to which I refer. The practical result which is of importance in questions affecting the condition of the inner layers of the earth is that we are not entitled—in fact, it is wrong—to suppose that pressure must necessarily go on raising the melting-point indefinitely; everything depends on the substance under consideration. It is therefore necessary to make such experiments as those of Tammann at vastly higher temperatures and pressures than those we have been considering, up to, probably, over 10,000 kilograms. per sq. cm. (or 63·5 tons per sq. inch).

In 1893 some experiments were described by Parsons (*Phil. Mag.*, xxxvi., 304) in which carbon rods were heated by electricity under a pressure usually of 15 tons per sq. inch—but rising in one case to 30 tons per sq. inch. The pressure was obtained by means of a hydraulic press, but no detail is given.

I have been desirous for many years of making some experiments at high temperatures and pressures, but for a long time could think of no way of ascertaining the pressure at temperatures over a red heat except by the use of compressed gases. In 1902 Sir August Noble was kind enough to have some drawings prepared for a wire-wound steel pressure vessel to carry a pressure of 50 tons per sq.

inch. The pressure was to be supplied by a compressed gas, and some details of the heating arrangements were designed, when a calculation of the cost of the gas compressors, vessel, and appurtenances made it clear that the undertaking would be beyond my means. I then endeavoured to find a simpler form of apparatus, and finally was led to contemplate the substitution of graphite for compressed gas, Spring having pointed out that crystalline graphite flows very easily at high pressures. A simple trial made it clear that the graphite of Ceylon does in fact possess the property of flowing like a liquid under high pressure to a sufficient degree to allow of pressure being transmitted by it. Graphite can be used with some reservation to transmit a pressure just like water or oil, though it is, of course, inferior in fluidity, and as I have now discovered occasions a loss of "head" which is not independent of the pressure itself. My former statement in the *Chemical Society Journal*, 1908, is erroneous, though the results of the experiments are, I believe, hardly or not at all affected by the mistake for a reason which will be clear later on. After several trials, the apparatus which I have here to-night was evolved, and some experiments were made with it. These experiments are not of any great importance, and, indeed, I felt almost ashamed of bringing them to your notice—I can only say in excuse that everything must have a beginning.

I believe, however, that the apparatus is sufficiently simple, cheap, and effective to enable others with more leisure at their disposal to make a beginning of an investigation of the properties of matter up to 100 tons per sq. inch, and at temperatures up to about 2000° C. At present, however, it is not possible to infer with accuracy the volume of the substance under these extreme conditions, nor can its physical condition be more than approximately and indirectly inferred—we must content ourselves with the production of transformations which we can make persist down to ordinary temperatures and pressures.

If we refer again to the sulphur diagram, we shall see how this possibility may arise. If sulphur is melted and cooled slowly, monoclinic crystals are found—when the temperature sinks below 98° C. these crystals undergo spontaneous transformation to the rhombic form—but all that we see is that the monoclinic crystals become opaque; the external form of the crystals is still monoclinic, but they are merely pseudomorphs of the original crystals. To obtain large octahedral crystals we may suppose that we begin by melting sulphur, and raising the temperature and pressure till the former stands at 160° C. or over, and the latter at not less than 1600 kg./cm.² (10·16 tons/sq. inch).

If we then slightly reduce the temperature or raise the pressure, we shall have the crystallisation of the sulphur in the rhombic form. By maintaining the pressure as the mass cools and when it is cold releasing the pressure, we should finally extract rhombic crystals. To this we may of course add that we need not expect crystals of any size unless we cool at the proper rate. It appears that there are at least two phenomena requiring attention in relation to the production of crystals—one is the relation between the amount of under-cooling necessary to induce spontaneous crystallisation, and the other is the rate at which the crystals will grow when they have once started. If we want large crystals we must not have an excessive number of points of spontaneous crystallisation; nor must we have too high a rate of crystal growth, or the crystals will by all experience tend to be felled together. The temperature condition giving birth to the most favourable number of spontaneous centres is not necessarily the temperature at which crystals grow to the largest size, so there is really no escape from finding by direct trial the most effective way to go to work.

Another possibility is brought to light by an examination of a case of pseudo-equilibrium such as that of phenol. Here we have three regions—in one No. 1 alone is stable, in another No. 2, and in the third both Nos. 1 and 2 are stable. The case of iodide of silver is similar but more complicated. If in the area C we change the pressure, the

* A Discourse delivered before the Royal Institution, March 19, 1909.

temperature remaining constant and the material consisting of a mixture of the two stable phases, we can alter the proportions in which these phases exist, but we cannot cause either of them to disappear.

A notable case of this kind is that of graphite and diamond, both perfectly stable in presence of each other at atmospheric pressure up to a temperature nearly that of the electric arc, say, about 3000°C . If there be any similarity between the carbon and phenol diagrams, diamond would correspond to variety No. 2 of phenol and graphite to variety No. 1, heat being evolved in both cases when the less dense modification changes into the denser. If we desire to obtain phenol 2 from phenol 1, we note that down to a temperature of -20°C ., we should require to keep the pressure always above about 600 kg./cm.^2 ; otherwise the operations would be similar to those described in the case of rhombic sulphur.

Similarly, to convert graphite to diamond on this analogy we should have to raise the temperature and pressure together to some unknown values and then let the product cool—keeping up the pressure meanwhile.

The apparatus which I have used in making the experiment is based on the transmission of pressure by crystalline graphite or the softer metals. In order to ascertain how much pressure is lost during transmission, I have arranged an apparatus in which the material to be tested is exposed to a known pressure, tending to force it through a cylindrical space, identical in figure with the space in which the heating is intended to be carried out. The pressure transmitted is transferred by a simple device to a piston with a hard steel point, and this is forced by the pressure to penetrate a soft steel plate. In a subsequent experiment, the same piston is forced by a known pressure into the same steel plate, so as to penetrate to the same depth as in the main experiment. It is then possible to compare the pressure transmitted with the pressure applied.

Experiments of this kind have been made with lead, and with graphite as pressure transmitting substances.

So far as I know, there is no substance other than graphite combining the property of a certain amount of fluidity with the capacity to resist high temperatures; and our hope of studying chemistry at really high pressures and temperatures appears at present to depend largely upon it. It is true that some attempts have been made to use compressed gases, but the apparatus is vastly more complicated, and the experiments themselves become really dangerous in view of the immense potential energy possessed by gases at pressures of 100 tons per square inch. As illustrating this I may mention that 100 tons per square inch is about the highest instantaneous pressure noted by Sir Andrew Noble in his well-known experiments on the exploding of cordite in closed vessels. The density of nitrogen at 100 tons per square inch is, taking Boyle's law as a very rough approximation, 15,240 times its density under standard conditions. This works out to rather over 19—i.e., about the same as gold, and the energy stored is of the same order as that contained in an equal volume of cordite, though its availability is lower.

The construction of the apparatus I have used can be easily followed from the drawings (Figs. 6 and 7). It consists essentially of a steel cylinder divided perpendicular to the longitudinal axis by a thin plate of mica; the two halves being clamped tightly together by an insulated ring, and clamps at top and bottom. Pressure can be applied by an ordinary hydraulic lifting jack—the one I have used will lift 50 or 60 tons—the bore of the hydraulic cylinder being about $4\frac{1}{2}$ inches. In order to operate at a high temperature, it is necessary to line the cylinder with some refractory substance, and I have generally used magnesia for this purpose, though zirconia or thoria might be better. Purified magnesia is first melted in an electric furnace, and then ground in an iron mortar till it is very fine. The powder is freed from iron as well as possible by a strong magnet, and after being sifted is pressed into the cylinder little by little by hydraulic pressure so as to form a solid plug. This is then bored out with a hard steel drill to the

required diameter. In pressing magnesia I have found that it is not possible to thoroughly consolidate the powder in greater thickness than a few millimetres, even under a pressure of 50 tons per square inch. In fact, magnesia is a substance which appears to be almost devoid of the fluid

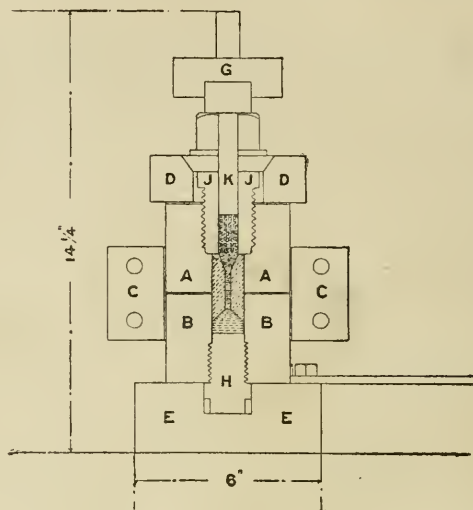


FIG. 6.

properties so marked in graphite—an essential condition for its use in the apparatus. I have tried various other linings, ground flint, alumina, &c., but they have no advantage over magnesia, and are even more difficult to drill out. Alumina prepared from the crystalline hydroxide

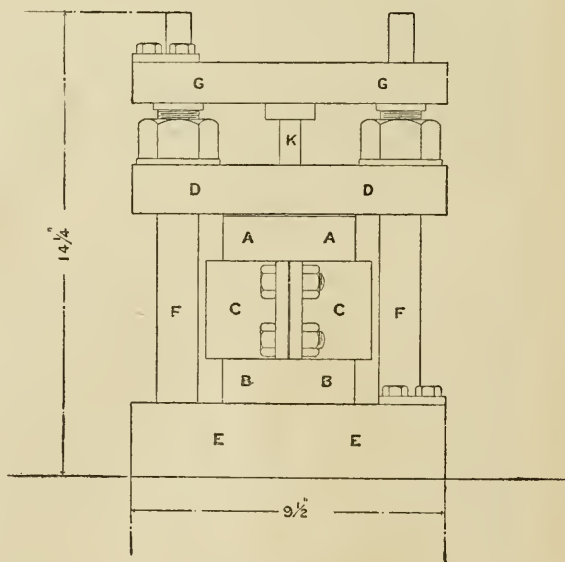


FIG. 7.

is very easily compressed into cakes, and makes a good lining, but it is too fusible for experiments on carbon, and is probably more easily reduced. The cylinder having been lined, the bottom is filled in with Acheson graphite in electrical communication with the base of the apparatus,

The substance to be operated upon is placed in the narrow part of the bore, and packed in with graphite or lead if that is suitable. The pressure is applied by a ram of hardened high speed steel, working upon a reservoir of graphite or lead contained in the plug closing the cylinder at the top, and electrically connected to the other terminal of the supply. The chief uncertainty in regard to the pressure which actually reaches the subject of the experiment lies in the possibility of the ram being held to some extent by friction against the side of the cylindrical hole in which it works, and in the consolidation of the graphite—with reduced fluidity, before it actually flows. One has to trust either to the hardness of the ram or to leave a space round it sufficient to allow graphite to escape, when the apparatus follows the lines of Amagat's standard pressure gauge, but the duration of the experiment is curtailed by the exhaustion of the graphite supply. A connection has to be applied for the pressure absorbed by the lead or graphite in accordance with the results of the preliminary trial. It is fair to say that no tendency of the ram to stick has ever been noticed—on the contrary, changes of volume brought about by heating have made themselves evident at once on the pressure gauge of the hydraulic press.

When working with any form of carbon there has been no trouble in arranging to heat the body which is being compressed by electrical means. It has been found most convenient to adjust the current to about the value required by means of a resistance—large compared with that of the pressure vessel—the latter being short-circuited meanwhile. In making an experiment, the hydraulic press is worked till the desired pressure is attained, and then by opening the switch the current is thrown on to the apparatus. When the magnesia lining begins to melt, the pressure, as shown by the pump gauge, is seen to fall, graphite flows into the magnesia tube, and the pump is worked so as to compensate for this. Under these conditions the pressure is probably transmitted without appreciable loss as the narrow part of the cylinder is now in a fluid bath. After a sufficient time has been allowed the switch is closed, and the pressure kept up by pumping till the apparatus is cold. Originally an apparatus with a cylinder made in one piece was employed, and in this case there was a considerable voltage between the graphite entering the apparatus and the steel walls of the pressure vessel. After a few seconds of intense heating it frequently happened that an explosion took place, due (as could be seen by subsequent examination), to filaments of graphite being driven through the magnesia and producing short circuits against the steel vessel. With the construction above described these explosions do not occur, and there is the additional and very real advantage that when an experiment is over the apparatus can be opened in the middle, and everything exposed to view.

A large number of experiments were made on different kinds of carbon and graphite. The weight of material in the highly heated part was generally from 1 to 2 grms., and the energy supply was at a rate of 5 to 10 kilowatts for from three to six seconds. The pressure in a successful experiment lay at from 50 to 100 tons per square inch throughout. The magnesia lining was usually melted for a distance up to 1 cm. round the graphite. Now magnesia melts at ordinary pressures at about 2000° C., but the energy supply is sufficient to render it possible that temperatures of from 3000° to 4000° C. may have been reached; it is possible that about 3000° C. was actually attained at the centre of the charge. The results obtained were uniform. No matter what form of carbon (excluding diamond, which was not tried), was packed originally in the apparatus, the final product was soft well-crystallised graphite, which agrees with some results of similar experiments described by Mr. Parsons (*Proc. Roy. Soc.*, 79), but not with the results claimed by Dr. Ludwig (*Zeit. für Electrochemie*, 1902, 273).

In several experiments the crystalline mass of graphite was tested in regard to its porosity, and this was found to

be considerable—a remarkable result, having in view the conditions under which it had been formed.

Another point of interest was that where the soft graphite had been driven into the Acheson graphite plug at the bottom of the apparatus it became extremely hard, so much so that a hard steel file made little or no impression upon it.

The main difference in treatment of this part of the graphite as compared with the remainder is that it was cooled much more quickly, thanks to the high heat conductivity of the Acheson graphite plug. The cause of hardening has hitherto not met with any satisfactory explanation.

No appreciable quantity of carbide of magnesia was formed in the experiments. The magnesia close to the graphite core contained traces of carbides, but as there were always traces of iron left from the drilling-out process, this may be plausibly accounted for by the formation of carbide of iron.

The graphite was finally systematically searched for microscopic diamonds by Staudenmaier's modification of Brodie's method of conversion of graphite into graphitic

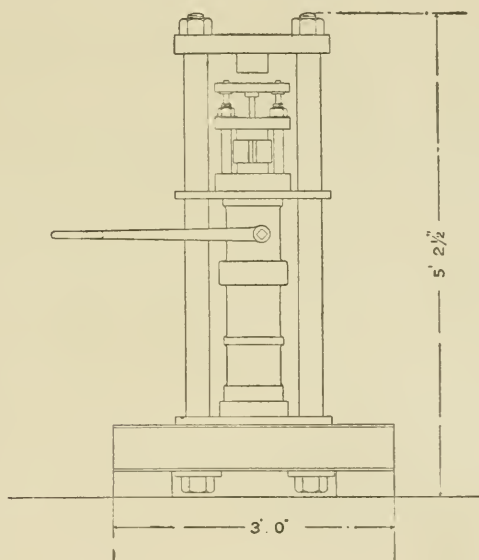


FIG. 8.

acid (*Ber.*, 1898, xxxi., 1485), or else by Moissan's modification of the same method ("Electric Furnace," 49, translation). A convenient means of distinguishing diamond in fine powder from most or all of the substances which are not separated by a liquid of density 3.34 at 4° C. is to heat the powder in a silver spoon to a dull red heat in fused potassium hydroxide. Check experiments showed that diamond dust easily passing a sieve with 100 threads to the inch would withstand the action of molten caustic potash at a temperature at which the edges of the silver spoon began to melt, for five or ten minutes. Crystals of alumina or of carborundum are entirely destroyed by this fusion, but the diamond particles seemed to have undergone no change. In fact, the individual fragments could be recognised under the microscope after passing through the ordeal.

I am led to consider that my experiments indicate that no wholesale transformation of amorphous carbon or graphite into diamond can be brought about by temperatures of the order of 2000° C., and pressures of more than 50 and less than 100 tons per square inch. There is some uncertainty, as already mentioned, in regard to the

actual pressures operative during the trials. Prof. Tammann has, however, obligingly drawn my attention to the fact that the equilibrium curve graphite-diamond may nevertheless have been crossed, but that no diamond was formed because time for crystallisation was not allowed under the conditions of the experiment. I confess my idea in making the trials was that the amorphous carbon or graphite might be forced to melt, and then that the conditions would require it to re-crystallise as diamond—not, of course, in the form of large clear crystals, but rather in the style of bort or black diamond. It is, however, true that the pressures used may have prevented any melting at all, and that it may have been a question of re-crystallisation of graphite, in which case the addition *ab initio* of diamond crystals would, as suggested by Prof. Tammann, have been of advantage in promoting crystallisation in that form.

The experiments described have only been rendered possible by the invention of high speed steel which keeps its hardness up to nearly or quite a red heat, and any further advance—mainly in the direction of the allowance of more time—must wait for improvements in that material. It may very well be, however, that the limits of temperature within which crystallisation in diamond form can take place, are really very narrow at any pressure—and in this case it will be a matter of very great difficulty to make an apparatus in which the conditions could be kept constant for a sufficient length of time—and the difficulty would be greater the higher the temperature.

It is noteworthy from this point of view that in Moissan's artificial production of diamond very much lower pressures and temperatures were used than those just described. I have shown (*Journ. Chem. Soc.*, 1908, xciii., 1351) that, using iron as a solvent, it is highly improbable that Moissan attained a pressure of more than 20 tons/sq. inch, and when silver was employed the pressure would be much lower. A similar criticism places the effective temperature of formation of diamond in iron or silver spheroids at something of the order of 1500° C. Comparing the experiments of Moissan with those described above, it looks as if Roozeboom's opinion is at present the most probable—viz., that solvents are necessary in order to depress the crystallisation point of diamond to a temperature at which the transformation to graphite is slow enough for rapid cooling to interrupt it. In this case the next step would be to repeat the experiments I have described at the highest possible pressure in the presence of iron, though Mr. Parsons (*loc. cit.*) has already made some trials in this direction with negative results. We have, however, many metals which have never been tried in this connection, and one or other of them may turn out to have the requisite properties.

I desire to acknowledge the assistance I have received in making the experiments described from my assistant Mr. C. H. Beasley, and in examining the products from Mr. T. H. Waller.

DETERMINATION OF FERROUS OXIDE IN MAGNETITE.

By R. B. GAGE.

THE various errors that may occur in the determination of ferrous iron by the Mitscherlich method or those of Pratt and Cooke, their causes and the necessary corrections, are discussed by Hillebrand so thoroughly that it is not necessary to deal with them all here (*U.S. Geological Survey Bulletin* No. 305, 1907, 131). However, since that caused by the action of the manganous salts on the permanganate is of special importance in certain cases studied by the writer, it will be considered in the present paper.

While making a series of analyses of magnetites containing from 25 to 30 per cent of ferrous oxide, the writer found it almost impossible to get good check results by any

of the hydrofluoric acid methods unless the excess of this acid was expelled. To drive off this excess of acid lengthens the time of the determination very much, increases the chances of oxidation, and introduces other objectionable conditions. The large amount of manganese introduced into the solution during titration makes the end reaction exceedingly difficult to secure. In fact, an excess of 5 cc. of the oxidiser would only give a passing colour.

The results secured by decomposing the ore with hydrochloric acid as recommended by some authorities are not only worthless in many cases, but the chlorine liberated soon ruins the platinum crucible. Only in the case of those ores which are known to contain no manganese in the dioxide state, and are completely decomposed by hydrochloric acid, is it safe to determine the ferrous iron by this method. Even then the results are not always above suspicion.

A few drops of permanganate added to a solution containing as much as 10 cc. of hydrofluoric acid will give a fairly permanent colour, but if some manganous sulphate is added the colour will disappear at once. If the substance under examination does not contain over 5 per cent of ferrous oxide, the amount of permanganate required to oxidise it will not introduce enough manganese into the solution to obscure the end-point to any marked degree. But as the ferrous oxide increases, the end-point becomes more and more difficult to secure.

This reduction of the permanganate after the iron has all been oxidised is caused by the action of the manganous fluoride. When vanadium is present it also will reduce some permanganate at this point, as vanadium oxidises much slower than iron.

If the solution could be freed of hydrofluoric acid, or the same rendered inert, there is no reason why the ferrous oxide could not be determined with as great a degree of accuracy in substances rich in this oxide as in those that contain but little of it.

It was found that the error caused by the excess of hydrofluoric acid in the solution could be decreased very much by adding sufficient calcium phosphate to the solution just before titrating to precipitate the fluorine as calcium fluoride. This renders the fluorine quite inert, and the end-point is fairly permanent. An excess of the calcium phosphate over what is required to precipitate the fluorine should always be added. When working on a half grm. of material, five grms. of calcium carbonate converted into the phosphate will be sufficient unless little or no hydrofluoric acid was expelled during solution of the material. When this happens more of the calcium phosphate should be used.

A series of ten determinations were run on a sample of magnetite, and the results secured are given below. The first five were made in the usual manner, while the calcium phosphate was used in the last five. A half grm. of material was used in each determination. Each cubic centimetre of permanganate represents 0.0025 gm. of iron.

No.	Cc. KMnO ₄ required.	Per cent of FeO.
<i>Without Ca Phosphate.</i>		
1.	41.6	26.74
2.	41.3	26.55
3.	41.5	26.67
4.	41.2	26.49
5.	41.3	26.55
<i>With Ca Phosphate.</i>		
6.	41.1	26.43
7.	41.0	26.37
8.	41.0	26.37
9.	41.1	26.43
10.	41.0	26.37

It is also a question whether anything is gained by reducing the material to an impalpable powder. In fact the material seems to cake quicker in the bottom of the crucible

when exceedingly fine, while little or no time is saved in decomposing it. It has also been shown that more or less oxidation of the ferrous iron takes place during this fine grinding (*Journ. Am. Chem. Soc.*, xxx., 1120). Material that does not contain grains larger than 0.08 mm. in diameter can usually be decomposed in about five minutes.

The method and apparatus used in the New Jersey Geological Survey laboratory to decompose the material are similar to that recommended by Pratt with a few modifications, and are described below.

A 50 cc. platinum crucible with a tight fitting lid is a very convenient size for this determination. A piece of thick card asbestos having an opening in the centre that will allow the crucible to pass about half way through is also required. This opening should form as nearly an air-tight opening as possible. A loop is made on the end of a stiff platinum wire, the diameter of the same being slightly larger than that of the opening in the asbestos board, so it will fit the crucible a little above the point where the crucible rests in the asbestos board. The wire is bent perpendicular to the plane of the loop, and should extend about two inches above the crucible when the latter rests in the loop.

A half grm. of the sample is weighed into the crucible. It should be thoroughly moistened with water and a couple of coils of fine platinum wire added to prevent bumping. The crucible is hung in the loop of platinum wire and lowered into the opening in the asbestos board. A cold mixture of 10 cc. of hydrofluoric acid and 15 cc. of dilute sulphuric acid (1:3) is added, and the crucible quickly covered. A 6-inch funnel, the top of which is connected with a CO₂ generator and the inside paraffin coated, is placed over the crucible. In case the funnel does not fit the asbestos board tightly, a little water poured around its base from time to time will keep the joint quite air-tight. If the generator is working vigorously, the enclosed air will be expelled in a few minutes. The chances of oxidation during this time are exceedingly small because the sample is attacked but little by the cold acid mixture. After the air has been expelled from the funnel, a Bunsen burner is placed beneath the crucible, the top being about three inches below its bottom. The flame is raised until it nearly touches the crucible and kept at this height until the contents have come to a boil, when it is lowered just enough so the liquid will continue to boil gently. If the heat is not sufficient to keep the material in motion, the heavy mineral particles may settle to the bottom of the crucible and escape decomposition. Also a much smaller per cent of the hydrofluoric acid will be expelled than otherwise. On the other hand, if too much acid and water are driven off, some of the salts will be forced out of solution. A reddish brown sediment in the bottom of the crucible that will dissolve when the solution is diluted should not be mistaken for undissolved material. An ordinary rock can usually be decomposed in five minutes. Magnetites and rocks rich in ferromagnesian minerals may take a little longer.

After the sample is completely decomposed, the burner is removed, and when the steam in the crucible has condensed, the lid of the crucible is held firmly in place with a glass rod while the crucible is raised by the platinum wire and plunged at once into a beaker containing from 400 to 500 cc. of cool boiled distilled water. The lid is kept in place until the beaker is placed beneath the burette ready for titrating. The contents of the crucible are quickly mixed with the excess of cold water, a solution containing the required amount of calcium phosphate added, and the titration executed as rapidly as possible. The first permanent colour is taken for the end-point, even if it does fade in a few moments. A few more drops should give a good colour if the addition of the oxidiser was stopped at the right point, and should always be added as a check. If the solution contains too much free sulphuric acid, no precipitate of calcium fluoride will appear on adding the calcium phosphate. The excess of acid used to decompose the material is sufficient for titrating, while

it is not enough to prevent the precipitation of the fluoride. It is not advisable to add the calcium phosphate before the contents of the crucible have been mixed with the large excess of cold water, as a dense precipitate may form in the crucible that might enclose some ferrous iron.

The writer has had little trouble in securing duplicate determinations that vary less than 0.1 cc. in a total consumption of 48 cc. of permanganate, the iron value of the same being 0.0025 grm. of metallic iron per cc. A blank determination should always be run and the corresponding correction made.

To prepare the calcium phosphate solution, suspend five grms. of calcium carbonate in 50 cc. of distilled water, and add 10 cc. of ortho-phosphoric acid (85 per cent) slowly while stirring.—*Journal of the American Chemical Society*, xxxi., No. 3.

THE DETERMINATION OF IODINE IN PROTEIN COMBINATIONS.

By LOUIS W. RIGGS.

THE recent progress of thyroid therapy, and the apparent relation between the quantity of iodine in thyroid preparations and their physiological action, have emphasised the importance of greater accuracy in the quantitative determination of iodine in protein combinations.

The method used by nearly all investigators for the determination of the amount of iodine in protein combination is that of Baumann (*Zeit. Physiol. Chem.*, xxii., 1), certain features of which were previously suggested by Rabourdin (*Ann. Chem.*, lxxvi., 375), and is briefly as follows:—

The iodine-containing protein is dried, powdered, and mixed in a large silver crucible with from two to three times its weight of solid sodium hydroxide and sufficient water to make a paste. The contents of the crucible are then cautiously heated to complete carbonisation, when sodium nitrate, in amount approximately equal to one-half the weight of the sodium hydroxide used, is added to completely oxidise the carbon. The fused mass is extracted with water, filtered, acidified with sulphuric acid, and shaken out with chloroform. The chloroform solution has a purple colour. The quantity of iodine is estimated colorimetrically by adding to solutions of sodium sulphate known quantities of potassium iodide, a few drops of a dilute solution of sodium nitrite, sulphuric acid to acid reaction, shaking out with an equal volume of chloroform, and comparing colours in equal sized cylinders.

Oswald (*Zeit. Physiol. Chem.*, xxiii., 265), upon Baumann's advice, employed a nickel instead of a silver crucible for the fusion, while Anten (*Arch. Exp. Path. Pharm.*, xlviii., 331) used carbon disulphide in place of chloroform on account of the rapid fading of the colour of dilute coloroform solutions of iodine.

The author's determinations of iodine in about sixty human thyroid glands, according to the foregoing process, indicated the desirability of further improvements of Baumann's method.

Unless otherwise stated, in all determinations to which reference is made in the following investigation, the protein, if dry, was fused with from two to two and one-half times its weight of solid sodium hydroxide in a nickel crucible. About one-fifth of the sodium hydroxide was added after the carbonisation, and immediately before adding sodium nitrate. The same weight of sodium hydroxide was used with 4 or 5 grms. of fresh tissue as with 1 grm. of dried tissue or dried protein. The fusion was conducted at a barely perceptible red heat, and the powdered sodium nitrate added gradually. The fused mass was cooled, extracted with water, and filtered, the crucible and filter repeatedly washed with hot water, the washings added to the extract, the latter made up to 100 cc., and thoroughly mixed. An aliquot part of this extract, usually 10 cc., was

placed in a small separator with 10 cc. of carbon tetrachloride, and cautiously acidified with 25 per cent sulphuric acid. (At the suggestion of Dr. Beebe, carbon tetrachloride was used instead of chloroform or carbon disulphide). After several thorough shakings with all possible care to avoid loss due to the escape of carbon dioxide, the carbon tetrachloride extract was filtered through a small filter previously moistened with carbon tetrachloride into a 10 cc. Nessler tube of carefully selected white glass, giving a column of liquid 10 cm. in length.

At first standards were made according to Baumann's method, but it was found that the quality of the colour of the carbon tetrachloride solution from the fused protein was often slightly different from that of the standards. In order that the standards might be prepared under conditions more nearly parallel to those of the extracts under examination, about 100 grms. of beef heart tissue were fused with sodium hydroxide and sodium nitrate, the fused mass extracted with water, filtered, and diluted. Standards were prepared by placing 5 or 10 cc. of this extract in a separator with 10 cc. of carbon tetrachloride and a known quantity of potassium iodide, sulphuric acid was then added to acid reaction, the carbon tetrachloride solution of the free iodine shaken out, and filtered into a 10 cc. Nessler tube, which must be precisely the same in shape and colour of glass as the tube containing the carbon tetrachloride solution of iodine from the protein under examination.

Is a Measurable Portion of Iodine Oxidised to Iodate during the Fusion Process?—This possibility was recognised by Baumann, but he stated that loss from such action would be avoided by removing the flame when carbonisation was completed, and immediately adding finely powdered sodium nitrate to the contents of the hot crucible. In attempting to follow this part of Baumann's procedure it was found necessary to heat the crucible to bright redness in order to obtain complete combustion of the carbon. Such a degree of heat, and the violent deflagration which occurs on the addition of the nitrate, although tending to reduce to iodide, would cause a loss of the latter by volatilisation. This procedure also requires a larger quantity of nitrate than is necessary if the latter be added gradually to the contents of the crucible maintained at a dull red heat.

In order to determine if any iodine as iodate remained in the acid aqueous liquid after shaking out with carbon tetrachloride, the liquid was again shaken with another 10 cc. of carbon tetrachloride to remove any traces of free iodine. This second portion of carbon tetrachloride was drawn off, the acid aqueous liquid placed in a small Kjeldahl flask with about 0.5 gm. of Devarda's alloy (*Zeit. Anal. Chem.*, xxxviii., 55; Al, 59; Cu, 39; Zn, 2 per cent), and made strongly alkaline with sodium hydroxide. A brisk action usually began at once, but in all cases heat was applied for about thirty seconds to insure a vigorous and complete reduction, and the flask with its contents allowed to stand over-night. (Experiments upon solutions of sodium iodate of known concentration showed reduction to be complete in about three hours). The liquid in the flask was then filtered into a separator. To the filtrate were added 10 cc. carbon tetrachloride, 1 cc. of 1 per cent solution of sodium nitrite, and 25 per cent sulphuric acid to strong acid reaction. The acid should be added until the precipitate which first formed is completely dissolved. After thorough shaking, the carbon tetrachloride was filtered into a 10 cc. Nessler tube, and read against standards made from a liquid containing the reduction products of Devarda's alloy, 1 cc. of a 1 per cent solution of sodium nitrite and known quantities of potassium iodide.

For comparison tubes Baumann used cylinders 20 cm. in length and of 100 cc. capacity. Ten cc. of chloroform would make a layer of liquid in such a cylinder about 2 cm. deep. Accordingly, he stated that he obtained the most satisfactory readings when 10 cc. of chloroform contained from 0.2 to 1.5 mgrm. of iodine. With the smaller tubes used by the writer, the best readings were obtained

when 10 cc. of carbon tetrachloride contained from 0.02 to 0.15 mgrm. of iodine. Quantities of iodine within these limits, in 10 cc. of carbon tetrachloride, were much more accurately read by the small Nessler tubes than by a Duboscq colorimeter.

The purpose of the analyses, of which the results are given in the following table, was to determine if iodine as iodate was left in the acid aqueous liquid after shaking out with carbon tetrachloride. Before applying the reduction process the acid aqueous liquid was shaken out with a second 10 cc. of carbon tetrachloride to remove any trace of free iodine left by the first extraction. This second extraction would be omitted in analyses if the object be to determine the total iodine, as any traces of free iodine left by the first extraction would be recovered along with that obtained by reduction.

One entire lobe of the gland was used for each analysis. They varied in weight as follows:—Beef thyroid lobes from 3.5 grms. to 33.0 grms. Pig thyroid lobes from 2.5 grms. to 13.5 grms. Sheep thyroid lobes from 2.1 grms. to 11.8 grms. The glands were selected at random from lots of 10 to 25 pounds received from abattoirs. Column I. gives the number of the analysis. Column II. the iodine found in mgrms. per gm. of fresh gland, and Column III. the percentage of total iodine found by the reduction process.

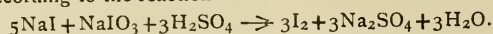
I.	II.	III.	I.	II.	III.
<i>Beef Thyroid.</i>					
1.	0.03	27.0	8.	0.41	7.2
2.	0.19	20.0	9.	0.02	2.0
3.	0.04	30.7	10.	0.61	6.6
4.	0.10	20.0	11.	0.70	2.3
5.	0.17	13.5	12.	0.45	5.6
6.	0.17	9.1	13.	1.47	2.6
7.	0.26	5.4	14.	1.07	6.3
<i>Pig Thyroid.</i>					
1.	1.04	0.0	5.	1.54	3.0
2.	0.65	0.0	6.	0.31	4.0
3.	1.34	trace	7.	0.65	2.4
4.	0.12	trace	8.	0.08	25.0
<i>Sheep Thyroid.</i>					
1.	0.03	77.0	4.	0.034	58.0
2.	0.013	72.0	5.	0.062	57.0
3.	0.034	55.0	6.	0.41	10.2

While our analytical results generally show that the less the quantity of iodine per gm. of fresh gland the greater the proportion oxidised to iodate, exceptions sometimes occur. Thus, a sample of tissue residue from human thyroid glands, which had been ground with sand and extracted several times with 0.8 per cent sodium chloride solution, and therefore was very poor in iodine, was roughly divided into two nearly equal portions, A and B, and the iodine determined.

	Iodine before reduction.	Iodine after reduction.	Total.
	Mgrms.	Mgrm.	Mgrms.
A ..	1.4	0.55	1.95
B ..	2.0	0.05	2.05

Although the total quantities of iodine in A and B agreed as closely as could be expected, it being impossible to divide the tissue equally, 28 per cent of the iodine in A was obtained by reduction, while only 2.4 per cent in B.

Iodides reduce iodates in the presence of sulphuric acid according to the reaction—



Disregarding at this point the action of nitrous acid, which is always present in the acidified fusion extract, it is evident that if the proportion of iodate be greater than one molecule of iodate to five molecules of iodide, some of the

iodine will remain as iodate after shaking out with carbon tetrachloride.

In the fusion process sodium nitrate is added in a quantity sufficient to produce a homogeneous melt free from particles of carbon. Under these conditions the extent of oxidation is entirely unmanageable.

From the results of these and many other analyses we conclude that more or less iodate is usually present, and that in an accurate determination of the iodine in protein combination it is never safe to omit the reduction feature of the method outlined in the foregoing pages. Inasmuch as the reduction process is applied to the acidified fusion extract after the determination of iodine has been made by the usual method, it in no way interferes with this method. Any iodine recovered by the reduction process would otherwise be thrown away.

Accuracy of the Reduction Process.—The reliability of the reduction process was tested as follows:—An alkaline fusion extract was prepared by fusing a protein free from iodine with sodium hydroxide and sodium nitrate. Eight solutions containing this fusion extract mixed with known quantities of iodide and iodate were made up to 100 cc. and numbered by a member of the laboratory staff. These solutions were examined for iodine precisely as in the case of aqueous fusion extracts from iodine containing proteins, with the following results:—

No.	Given.			Found		
	Iodine as iodide.	Iodine as iodate.	Total.	Before reduction.	After reduction.	Total.
	Mgrm.	Mgrm.	Mgrm.	Mgrm.	Mgrm.	Mgrm.
1.	0.35	0.3	0.65	0.41	0.22	0.63
2.	0.25	0.4	0.65	0.3	0.33	0.63
3.	0.4	0.5	0.9	0.55	0.3	0.85
4.	0.5	0.8	1.3	0.75	0.55	1.3
5.	0.15	0.4	0.55	0.35	0.2	0.55
6.	0.9	0.2	1.1	0.85	0.2	1.05
7.	0.45	0.55	1.0	0.65	0.3	0.95
8.	1.0	0.25	1.25	0.95	0.28	1.23

That the reduction feature of this method is quite accurate is shown by a comparison of the figures in the fourth and seventh columns of the foregoing table.

Attempt to Reduce Iodate with Nitrous Acid.—Twenty-five grms. of beef heart tissue were fused with 17 grms. of sodium hydroxide and sufficient sodium nitrate to oxidise the carbon. The fused mass was extracted with water, the extract filtered, and made up to 250 cc. Ten cc. of this fusion extract gave by the permanganate method 0.15 mgrm. of sodium nitrite. Ten cc. of the fusion extract with 10 cc. of carbon tetrachloride, and 0.2 mgrm. of iodine as sodium iodate were placed in each of four separators; the contents of each separator strongly acidified with 25 per cent sulphuric acid, and shaken at frequent intervals for one and one-half hours. On comparison with standards it was found that the largest reduction of any of the four samples was equivalent to 0.05 mgrm. of iodine, or only one-fourth of the iodine present.

Ten cc. of a fusion extract—prepared as in the last experiment but containing 0.21 mgrm. of sodium nitrite in 10 cc.—were placed with 10 cc. of carbon tetrachloride in each of eight separators. Iodine as sodium iodate was added to the contents of the separators as follows:—Nos. 1 and 2 received 0.05 mgrm., 3 and 4 received 0.1 mgrm., 5 and 6 received 0.15 mgrm., and 7 and 8 received 0.2 mgrm. The contents of each separator were made strongly acid with 25 per cent sulphuric acid, and shaken vigorously at frequent intervals. Ten minutes after the first shaking Nos. 1 to 4 gave no colour, Nos. 5 to 8 gave a very slight colour. One hour later, with frequent shaking, Nos. 1 to 4 showed a slight colour; Nos. 5 and 6 gave a colour equivalent to 0.04 mgrm. of iodine; Nos. 7 and 8 gave 0.05 mgrm. of iodine. All smelled of nitrous fumes. After three hours there was no apparent change in colour. The next day all colours had faded as compared with standards made from solutions of potassium iodide,

sodium sulphate, and 0.01 grm. of sodium nitrite in 10 cc., and which had been allowed to stand the same length of time. Nos. 2, 4, 6, and 8 were then made alkaline with sodium hydroxide, reduced with Devarda's alloy, and the balance of the iodine recovered without difficulty.

Ten cc. of a fusion extract containing 0.15 mgrm. of sodium nitrite were mixed in a separator with 10 cc. of carbon tetrachloride, 0.2 mgrm. of iodine as sodium iodate, and 25 per cent sulphuric acid to strong acid reaction. Immediately after shaking, the carbon tetrachloride showed but a trace of colour equivalent to not more than 0.01 mgrm. A 1 per cent solution of sodium nitrite was then added to the contents of the separator in portions of 1 cc. each, with vigorous shaking between each addition. Three cc. of sodium nitrite developed a colour equivalent to about 0.05 mgrm. of iodine, or one-fourth of the quantity present. The colour of the tetrachloride was brownish, and impossible to read accurately. Two cc. more of the nitrite solution and 1 cc. of 25 per cent sulphuric acid caused dense brown fumes above the liquid in the separator.

Nitrous acid fails to reduce iodates quantitatively to iodine so that the latter can be measured colorimetrically.

Ten cc. of a fusion extract containing 0.15 mgrm. of sodium nitrite were mixed in a separator with 10 cc. carbon tetrachloride, 0.1 mgrm. of iodine as potassium iodide, and 25 per cent sulphuric acid to acid reaction. The colour immediately after shaking was equivalent to 0.1 mgrm. of iodine. To the contents of the separator 1 cc. of a 20 per cent solution of sodium nitrite was added and mixed thoroughly, whereupon the colour of the tetrachloride changed to salmon. Another cc. of the sodium nitrite caused a further loss of colour, and 4 cc. of 20 per cent sodium nitrite completely discharged the purple colour of the carbon tetrachloride. A repetition of this experiment with double the quantity of iodine gave parallel results.

Not only does nitrous acid fail to reduce iodates so that the iodine can be read colorimetrically, but sufficient excess of the acid will decolorise a solution of iodine in carbon tetrachloride. It was also found that nitrous acid would modify or discharge the colour of a carbon disulphide solution of iodine.

Analyses of Mixed Iodide and Proteid.—Baumann tested his process by mixing known quantities of potassium iodide with fibrin, and subjecting the mixture to analysis by the method employed for the determination of iodine in thyroid glands. About 90 per cent of the iodine was recovered by analysis.

In order to test the details of the process as employed by the author, analyses were made of thirty mixtures of potassium iodide with fibrin. The concentration varied from 0.45 to 4.0 mgrms. of iodine as potassium iodide to 1 grm. of dried fibrin. In the majority of these analyses, 90 per cent or more of the iodine was recovered before reduction, and traces or none by the reduction process. In general, the greater the concentration of the iodine the less obtained by reduction. Mixtures containing 2 or more mgrms. of iodine as potassium iodide with 1 grm. of fibrin yielded 95 per cent of their iodine without reduction. Two out of the thirty mixtures gave exceptional results, namely, 20 and 30 per cent of their iodine by reduction.

The analyses of ten mixtures of fresh beef pancreas tissue with varying quantities of iodine as potassium iodide, gave results closely agreeing with those obtained from the analysis of mixtures of fibrin and potassium iodide.

It is evident that iodine as potassium iodide mixed with a proteid is not oxidised by fusion with sodium hydroxide and sodium nitrate to the same extent as iodine in combination with a proteid, such as the iodine-containing constituent of the thyroid gland.

The fact that iodine-containing proteids, especially those containing small quantities of iodine, do not yield all of their iodine by Baumann's process, throws doubt upon the accuracy of results heretofore announced with reference to the iodine content of protein substances.

The modifications of Baumann's process suggested in this paper still leave much to be desired. It is therefore my intention to continue the study of the problem, especially the fusion and reduction features.

Summary.

Ten cc. Nessler tubes of clear white glass, and giving a column of liquid 10 cm. in length, yield more delicate readings with dilute solutions of iodine in carbon tetrachloride than larger sized tubes or a Dubosq colorimeter.

A portion of the iodine is oxidised to iodate during the fusion, and may be lost unless subsequently reduced. Devarda's alloy was used as the reducing agent. The reduction is particularly necessary in the analysis of proteins containing but a small proportion of iodine.

Excess of nitrous acid fails to reduce iodates so that the iodine can be estimated colorimetrically in carbon tetrachloride solution, and a sufficient excess of nitrous acid will modify or discharge the colour of a carbon tetrachloride solution of iodine. Too great a quantity of sodium nitrate must not be added during the fusion, or an excess of nitrous acid will be formed upon acidifying.

Mixtures of protein substances and potassium iodide subjected to analysis by the foregoing process do not give results comparable with those obtained from the analysis of a protein substance containing combined iodine, such as thyroid gland tissue.

Extreme care must be used to make the conditions under which standards are prepared and read parallel to those to which the substance under examination is subjected. Reductions and colorimetric readings should be made in duplicate or triplicate, and repeated, if necessary, until concordant results are obtained.

The writer wishes to express his thanks to Dr. S. P. Beebe for much of the material upon which this investigation was made, and for his hearty encouragement throughout the work.—*Journal of the American Chemical Society*, xxxi., No. 6.

THE OXIDATION OF PHENOL.*

THE EFFECT OF SOME FORMS OF LIGHT AND OF ACTIVE OXYGEN UPON PHENOL AND ANISOLE.

By H. D. GIBBS.

Concluded from p. 83).

Experimental.

Two soda-glass tubes, 60 cm. long and 16 mm. inside diameter, the glass less than 1 mm. in thickness, were thoroughly dried and sealed, inclosing an atmosphere of pure dry oxygen, free from ozone and gas ions, and placed in the direct sunlight. The moisture was removed from the tubes by sealing them on to the drying chain (see Fig. 1) previously described, at the point *b*, and the chain was closed to moisture by a phosphorus pentoxide tube sealed on at the right extremity. All of that portion of the apparatus inclosed between the phosphorus pentoxide tubes was heated to 110° for six hours in a current of oxygen. The ozone was removed from the oxygen by the combustion furnace and the gas ions were destroyed by the tube of tightly packed glass wool G (Thomson and Rutherford, *Phil. Mag.*, 1896, xlii., 392). After cooling in the oxygen current and standing eighteen hours, the operation was repeated and the tube sealed out of the chain.

A second tube of the same dimensions was treated in the same way, except that before sealing it was opened just in front of the phosphorus pentoxide tube, the oxygen current running at a fairly rapid rate, and a small piece of cleaned and ignited silver foil inserted. The seal was then made several centimetres back from the opening to avoid

the introduction of moisture from the flame of the blow-pipe. One end of the tube was wrapped with tin foil for a distance of 5 cm. and the pieces of silver put into this darkened pocket so that the direct rays of the sun would not strike it.

Silver foil discolours in the presence of ozone (Thiele, *Zeit. Chem.*, 1906, xii., 11); the test, however, is not as delicate as some others.

After four and ten days' exposure respectively, the tubes were removed from the direct sunlight at 1 p.m. to obtain the maximum sun effect, and immediately tested for ozone. The first tube was cooled to produce a slightly reduced pressure in the interior, so that on breaking the tip beneath the surface of a sensitive potassium iodide and starch solution about 2 cm. were drawn in. This solution was passed repeatedly from end to end of the tube and showed no visible coloration on standing in the dark after twenty-four hours. The second tube was tested by breaking the tips from both ends and washing out the gas through the small opening by means of a stream of pure oxygen. The issuing gas played against a piece of sensitive potassium iodide-starch paper without producing any noticeable discoloration. The piece of silver foil also was without indication of ozone. If active oxygen was formed in the sunlight under the conditions described, the amount was so minute that the delicate tests employed were decidedly negative.

The Effect of Ozone and Oxygen and Sunlight upon the Methyl Ether of Phenol Anisole.

Anisole is not coloured by a rapid current of ozonised oxygen bubbling through it for two days at 30°, or by exposure to direct sunlight in the presence of moisture and oxygen for two months, the temperature occasionally rising above 40°.

No special attempts were made to purify the anisole. A sample which had been in this laboratory for some time was distilled once and the middle fraction employed in the experiments. It remained practically colourless throughout the experiments. The fixation of the labile hydrogen atom of phenol prevents oxidation under the conditions of the experiment.

The Activity of the Phenol Molecule.

The measurements of the absorption-spectrum of phenol made by Hartley (*Journ. Chem. Soc.*, London, 1902, lxxxi., 929) show a broad absorption band with a maximum at $\lambda = 272 \mu\mu$. The breadth of this band depends upon the concentration. With 1 mgrm. molecule in 100 cc. of alcohol the extremities of the band are $\lambda = 291.6$ to $243.1 \mu\mu$, and with 1 mgrm. molecule in 500 cc. they are $\lambda = 283.5$ to $261.5 \mu\mu$.

Anisole shows the same absorption band, with the difference that it divides into two bands near the head. This variation shows a marked difference between the constitution of the two compounds which has been traced by Baly and Collie (*Journ. Chem. Soc.*, 1905, lxxxvii., 1339) to a certain amount of tautomerism in phenol. The absorption band heading at about $\lambda = 277 \mu\mu$ is characteristic of the labile hydrogen atom. Baly and Eubank state (*Journ. Chem. Soc.*, 1905, lxxxvii., 1348) "These results leave no doubt but that phenol, under these experimental conditions, has not the same structure as anisole, and that the difference is due to the wandering of the labile phenolic hydrogen atom."

The active wave lengths are thus seen to be very close to the limit of the sun's rays which escape absorption in the atmosphere and which are capable of penetrating glass. The fact that the coloration of phenol has been found to be more rapid under quartz than under other kinds of glass is evidence upon this point. The failure of Kohn and Fryer (*loc. cit.*) to obtain any coloration of pure phenol is evidently due to the atmospheric conditions in Liverpool. In Manila, where this investigation has been carried on, the atmosphere is free from smoke, and very clear at certain seasons of the year. The altitude of the

* Contributions from Laboratory for the Investigations of Foods and Drugs, Bureau of Science, Manila, P.I. From the *Philippine Journal of Science*, vol. iv., No. 2.

sun is such that the ultra-violet absorption of the atmosphere is less than in Liverpool, even if the atmospheres in the localities were equally clear. Hartley (*Journ. Chem. Soc.*, 1881, xxxix., 111) says:—

"I have been led to attribute the limited extent of the solar spectrum, as photographed in London, to the selective absorption of rays by the tarry matters in the smoke of the town's atmosphere, especially since my experience of the extraordinary absorptive power of benzene derivatives."

That the phenol molecule is activated under the conditions of the observations described, appears to be a more reasonable explanation of the phenomenon than that the oxygen molecule is activated by available wave lengths which do not approach the region of the oxygen absorption spectrum. ("In the case of moist phenol, where there is hydrogen peroxide formation, other considerations enter"). In expounding the second law of Grotthuss—"the action of a ray of light is analogous to that of a voltaic cell" (*Journ. Phys. Chem.*, 1908, xii., 212),—Bancroft (*Journ. Phys. Chem.*, 1908, xii., 258) says:—

"If the active light is light which is absorbed by the substance to be oxidised and not by the oxygen, then the substance to be oxidised has been made active by the light and the oxygen is the depolariser. If the active light is absorbed by oxygen and not by the substance to be oxidised, then this latter is the depolariser and the oxygen is made active by light."

Eder ("Photochemie," Halle-a-S., 1906, 43) with regard to this phase of the question states that a compound which is acted upon by light absorbs only those vibrations of the light with which its atoms vibrate, or are capable of vibrating, in synchrony. In this way the absorption of the light is connected with the intra-molecular constitution of the compound. The amplitude of the vibrating atoms composing a molecule of a substance sensitive to light may be increased by the light waves vibrating in coincidence, and when a certain limit is exceeded, a breaking of the molecular bonds ensues; that is, photo chemical decomposition takes place. This effect is well exemplified by certain colour substances employed in photography to increase the optical sensibility of the silver salts ("Photochemie," Halle-a-S., 1906, 45). Bancroft says (*loc. cit.*, 360), concerning the action of optical sensitizers on photographic plates:—

"The theory of Grotthuss enables us to make a definite statement in regard to sensitizers, and one that differs to a certain extent from any of the previous ones. A sensitizer must be a depolariser, directly or indirectly. It must be a reducing agent in the broad sense of the term, or it must be changed into one by the action of light. In either case the sensitizer is decomposed by the action of light on the sensitised plate;" and "Eder's theory of molecular vibration cannot account for Abney's experiment with cyanine plates to which the silver bromide was added after the exposure to light" (*Ibid.*, 376).

The possibility that ozone is formed during the combination of phenol with oxygen is not excluded. From the fact that small amounts of carbon dioxide have been found in the tubes of pure phenol and purified atmospheric air after exposure in the sunlight until the major portion of the oxygen had disappeared, it seems to be quite possible that the sunlight reaction produces in a measure the same products as the reaction between ozone and phenol in the absence of light. It is also possible that a peroxide, other than hydrogen peroxide, is formed during the reaction.

The Effect of Temperature upon the Activity of the Phenol Molecule.

Kohn and Fryer have observed that the phenol residues in the distilling flasks are always coloured.

They state (*loc. cit.*, 108):—"The sample was therefore carefully distilled six times successively from a glass retort and the distillate collected in a glass receiver. The first portion of the distillate was always rejected, and a small residue left in the retort in each distillation. The residue left in the retort always possessed a dark pink tinge, which

darkened rapidly on exposure, even in blue glass bottles"; and on page 110, "The combined results of the previous series of experiments show that distillation from glass vessels is really an effectual means for completely purifying phenol. For our further experiments we therefore distilled 'absolute' phenol under the conditions already described, and in order to be well on the safe side fifteen successive distillations were made. The final product, which was quite colourless, melted at 41° C. . . . During the distillations the residue in each case turned pink, and on standing became red."

I have many times observed the same phenomenon on distilling phenol when access to the atmospheric air or oxygen was possible. When the phenol was distilled in an atmosphere of hydrogen with the apparatus shown in Fig. 1, the residues were always absolutely colourless when viewed by the eye. No precautions are necessary to exclude light, and the phenol in the hydrogen atmosphere will remain colourless indefinitely in the sunlight.

Experimental.

About 50 grms. of pure phenol were introduced into a distilling flask which was arranged with a tube reaching to the bottom, sealed in at the top of the neck. The phenol from the time of its purification was protected from the light and from contact with substances which might introduce impurities, and the distilling flask was likewise protected from the diffused daylight of the room by asbestos wrappings. No corks or stoppers were used in the distilling flask, glass seals only being employed. The sample was distilled with a current of purified, dry, atmospheric air slowly bubbling through the tube reaching to the bottom of the flask. The air was purified by passing through the purifying chain Fig. 1 previously described, with the combustion furnace heated.

The distillation was stopped when about 10 cc. of phenol remained in the distilling flask. The phenol had been at the boiling temperature twenty minutes, and during this time had assumed a light reddish yellow colour, about the shade usually produced by a few hours' exposure in contact with atmospheric air to the sun at a temperature of about 40°. On changing the air current to oxygen, and heating to the boiling-point, the rate of coloration was much more rapid, a brilliant red being produced in a few minutes.

A tube of pure dry phenol, prepared by the method of distillation in hydrogen in the apparatus described, shown by Fig. 1, and sealed in contact with purified atmospheric air, was protected from the action of light by heavy wrappings of tin foil, and placed in a steam bath at 100° in the dark. The steam bath was heated for seven hours a day during six days of the week. The tin foil covering was carefully removed once a week for the shortest possible length of time to allow examination of the phenol. At the end of the second week a faint reddish yellow was observed. This colour deepened constantly as time proceeded.

The rate of combination of the phenol molecule with oxygen, and consequently the formation of the colour, will undoubtedly be augmented with a gas mixture containing a higher percentage of oxygen than atmospheric air.

It is evident from these experiments that for the production of the purest phenol the distillation should not be conducted with access to oxygen. While the temperature of the phenol is elevated it should come in contact only with an indifferent gas. It is also probable that the combination with oxygen goes on at all temperatures down to the absolute zero, the temperature being an important factor of the rate.

Influence of the Altitude of the Sun upon the Rate of Coloration.

I believe that I have noticed a difference in the rate of coloration of phenol at different seasons of the year. When the sun is directly overhead, which occurs twice a year in this latitude, there is apparently a more rapid production of the red colour than when it is in the far south in December and January. This observation is attended by so many factors that it is difficult at this time to make

any positive statement. A more complete series of observations and measurements extending over a long period of time will be necessary before any definite results can be obtained.

It is obvious that the rays pass through a thinner layer of atmosphere in reaching the surface of the earth when the sun is in the zenith, and therefore the ultra-violet absorption will vary at different seasons of the year, and since the shorter wave lengths undergo refraction to a lesser extent than the longer, a greater proportion of the shorter waves reach the earth's surface when the sun is directly overhead.

It is possible that these considerations produce different light effects in the Tropics, where the sun is sometimes in the zenith, than in the temperate and arctic zones where it never reaches the same condition. ("The attempt to photograph the sun spectrum to shorter wave lengths than any recorded will shortly be made in this locality by the writer).

The admirable observations of Cornu have shown that the limit of the sun's spectrum is variable, according to the state of the atmosphere and the altitude of the sun (*Comptes Rendus*, 1879, lxxxviii., 1101), and that the longest ultra-violet spectrum was obtained near noon at the highest elevations (*Comptes Rendus*, 1879, lxxxix, 808).

Summary.

1. Pure phenol remains colourless in the sunlight when in contact with the indifferent gases, hydrogen, nitrogen, and carbon dioxide.

2. Pure phenol will become coloured in the presence of oxygen.

In the dark the rate is not appreciable at room temperatures. It increases with rise of temperature, can be measured at 100°, and at the boiling-point of phenol is fairly rapid.

In the sunlight the rate of coloration is rapid, and increases directly with the temperature.

3. The cause of the colour is oxidation.

The principal products of the oxidation are quinol, quinone, and catechol. Some carbon dioxide has been found.

The principal coloured compounds are probably quinone condensation products. The formation of the intense red condensation product phenquinone is probable.

4. Active oxygen will unite with phenol with considerable ease and rapidity.

Ozone is very reactive. Quinol, quinone, catechol, glyoxylic acid, and carbon dioxide have been identified among the products of the action with ozone. No ozonide has been isolated.

Oxygen liberated at the anode reacts with phenol. Quinone is one of the reaction products.

5. The experiments argue against the chemical activity of the oxygen gas ions.

6. The glass through which the sunlight acts upon phenol in the presence of oxygen has an influence upon the rate of reaction. Glasses having the most complete ultra-violet absorption retard the reaction in the greatest degree.

7. Ozone could not be detected in pure dry molecular oxygen sealed in a glass tube and exposed to the sun.

8. The altitude of the sun, the thickness of the atmosphere through which it acts, and the atmospheric conditions undoubtedly influence the rate of the coloration of phenol.

9. The methyl ether of phenol, anisole, is not coloured by ozone or oxygen and sunlight.

The fixation of the labile hydrogen of phenol decreases the susceptibility of the compound to oxidising influences.

10. The reactivity of the phenol molecule is augmented by the absorbed wave lengths at about $\lambda = 291$ to 243μ , and as far as has been observed the same effect is produced by higher temperatures. The oxidation and consequent coloration of phenol goes on under both influences.

11. The purest phenol can only be distilled out of contact with oxygen. Hydrogen has been employed in this work.

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THE CHEMICAL NEWS.

VOL C., No. 2596.

BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

WINNIPEG, 1909.

INAUGURAL ADDRESS OF THE PRESIDENT,
Prof. Sir J. J. THOMSON, M.A., LL.D., D.Sc., F.R.S.

TWENTY-FIVE years ago a great change was made in the practice of the British Association. From the foundation of our Society until 1884 its meetings had always been held in the British Isles; in that year, however, the Association met in Montreal, and a step was taken which changed us from an Insular into an Imperial Association. For this change, which now I think meets with nothing but approval, Canada is mainly responsible. Men of science welcome it for the increased opportunities it gives them of studying under the most pleasant and favourable conditions different parts of our Empire, of making new friends; such meetings as these not only promote the progress of science, but also help to strengthen the bonds which bind together the different portions of the King's Dominions.

This year, for the third time in a quarter of a century, we are meeting in Canada. As if to give us an object lesson in the growth of Empire, you in Winnipeg took the opportunity at our first meeting in Canada in 1884 to invite our members to visit Manitoba and see for themselves the development of the Province at that time. Those who were fortunate enough to be your guests then as well as now are confronted with a change which must seem to them unexampled and almost incredible. Great cities have sprung up, immense areas have been converted from prairies to prosperous farms, flourishing industries have been started, and the population has quadrupled. As the President of a scientific association I hope I may be pardoned if I point out that even the enterprise and energy of your people and the richness of your country would have been powerless to effect this change without the resources placed at their disposal by the labours of men of science.

The eminence of my predecessors in the chair at the meetings of the British Association in Canada makes my task this evening a difficult one. The meeting at Montreal was presided over by Lord Rayleigh, who, like Lord Kelvin, his colleague in the chair of Section A at that meeting, has left the lion's mark on every department of physics, and who has shown that, vast as is the empire of physics, there are still men who can extend its frontiers in all of the many regions under its sway. It has been my lot to succeed Lord Rayleigh in other offices as well as this, and I know how difficult a man he is to follow.

The President of the second meeting in Canada—that held in 1897 at Toronto—was Sir John Evans, one of those men who, like Boyle, Cavendish, Darwin, Joule, and Huggins, have, from their own resources and without the aid derived from official positions or from the universities, made memorable contributions to science; such men form one of the characteristic features of British science. May we not hope that, as the knowledge of science and the interest taken in it increase, more of the large number of men of independent means in our country may be found working for the advancement of science, and thereby rendering services to the community no less valuable than the political, philanthropic, and social work at which many of them labour with so much zeal and success?

I can, however, claim to have some experience of, at any rate, one branch of Canadian science, for it has been my privilege to receive at the Cavendish Laboratory many

students from your universities. Some of these have been holders of what are known as the 1851 scholarships. These scholarships are provided from the surplus of the Great Exhibition of 1851, and are placed at the disposal of most of the younger universities in the British Empire, to enable students to devote themselves for two or three years to original research in various branches of science. I have had many opportunities of seeing the work of these scholars, and I should like to put on record my opinion that there is no educational endowment in the country which has done or is doing better work.

I have had, as I said, the privilege of having as pupils students from your universities as well as from those of New Zealand, Australia, and the United States, and have thus had opportunities of comparing the effect on the best men of the educational system in force at your universities with that which prevails in the older English universities. Well, as the result, I have come to the conclusion that there is a good deal in the latter system which you have been wise not to imitate. The chief evil from which we at Cambridge suffer and which you have avoided is, I am convinced, the excessive competition for scholarships which confronts our students at almost every stage of their education. You may form some estimate of the prevalence of these scholarships if I tell you that the colleges in the University of Cambridge alone give more than £35,000 a year in scholarships to undergraduates, and I suppose the case is much the same at Oxford. The result of this is that preparation for these scholarships dominates the education of the great majority of the cleverer boys who come to these universities, and indeed in some quarters it seems to be held that the chief duty of a schoolmaster, and the best test of his efficiency, is to make his boys get scholarships. The preparation for the scholarship too often means that about two years before the examination the boy begins to specialise, and from the age of sixteen does little else than the subject, be it mathematics, classics, or natural science, for which he wishes to get a scholarship; then, on entering the university, he spends three or four years studying the same subject before he takes his degree, when his real life work ought to begin. How has this training fitted him for this work? I will take the case in which the system might perhaps be expected to show to greatest advantage, when his work is to be original research in the subject he has been studying. He has certainly acquired a very minute acquaintance with his subject—indeed, the knowledge possessed by some of the students trained under this system is quite remarkable, much greater than that of any other students I have ever met. But though he has acquired knowledge, the effect of studying one subject, and one subject only, for so long a time is too often to dull his enthusiasm for it, and he begins research with much of his early interest and keenness evaporated. Now there is hardly any quality more essential to success in research than enthusiasm. Research is difficult, laborious, often disheartening. The carefully designed apparatus refuses to work, it develops defects which may take months of patient work to rectify, the results obtained may appear inconsistent with each other and with every known law of Nature, sleepless nights and laborious days may seem only to make the confusion more confounded, and there is nothing for the student to do but to take for his motto "It's dogged as does it," and plod on, comforting himself with the assurance that when success does come, the difficulties he has overcome will increase the pleasure—one of the most exquisite men can enjoy—of getting some conception which will make all that was tangled, confused, and contradictory clear and consistent. Unless he has enthusiasm to carry him on when the prospect seems almost hopeless and the labour and strain incessant, the student may give up his task and take to easier, though less important, pursuits.

I am convinced that no greater evil can be done to a young man than to dull his enthusiasm. In a very considerable experience of students of physics beginning research, I have met with more—many more—failures from

lack of enthusiasm and determination than from any lack of knowledge or of what is usually known as cleverness.

This continual harping from an early age on one subject, which is so efficient in quenching enthusiasm, is much encouraged by the practice of the colleges to give scholarships for proficiency in one subject alone. I went through a list of the scholarships awarded in the University of Cambridge last winter, and, though there were 202 of them, I could only find three cases in which it was specified that the award was made for proficiency in more than one subject.

The premature specialisation fostered by the preparation for these scholarships, injures the student by depriving him of adequate literary culture, while when it extends, as it often does, to specialisation in one or two branches of science, it retards the progress of science by tending to isolate one science from another. The boundaries between the sciences are arbitrary, and tend to disappear as science progresses. The principles of one science often find most striking and suggestive illustrations in the phenomena of another. Thus, for example, the physicist finds in astronomy that effects he has observed in the laboratory are illustrated on the grand scale in the sun and stars. No better illustration of this could be given than Professor Hale's recent discovery of the Zeeman effect in the light from sunspots; in chemistry, too, the physicist finds in the behaviour of whole series of reactions illustrations of the great laws of thermodynamics, while if he turns to the biological sciences he is confronted by problems, mostly unsolved, of unsurpassed interest. Consider for a moment the problem presented by almost any plant—the characteristic and often exquisite detail of flower, leaf, and habit—and remember that the mechanism which controls this almost infinite complexity was once contained in a seed perhaps hardly large enough to be visible. We have here one of the most entrancing problems in chemistry and physics it is possible to conceive.

Again, the specialisation prevalent in schools often prevents students of science from acquiring sufficient knowledge of mathematics; it is true that most of those who study physics do some mathematics, but I hold that, in general, they do not do enough, and that they are not as efficient physicists as they would be if they had a wider knowledge of that subject. There seems at present a tendency in some quarters to discourage the use of mathematics in physics; indeed, one might infer, from the statements of some writers in quasi-scientific journals, that ignorance of mathematics is almost a virtue. If this is so, then surely of all the virtues this is the easiest and most prevalent.

I do not for a moment urge that the physicist should confine himself to looking at his problems from the mathematical point of view; on the contrary, I think a famous French mathematician and physicist was guilty of only slight exaggeration when he said that no discovery was really important or properly understood by its author unless and until he could explain it to the first man he met in the street.

But two points of view are better than one, and the physicist who is also a mathematician possesses a most powerful instrument for scientific research with which many of the greatest discoveries have been made; for example, electric waves were discovered by mathematics long before they were detected in the laboratory. He has also at his command a language clear, concise, and universal, and there is no better way of detecting ambiguities and discrepancies in his ideas than by trying to express them in this language. Again, it often happens that we are not able to appreciate the full significance of some physical discovery until we have subjected it to mathematical treatment, when we find that the effect we have discovered involves other effects which have not been detected, and we are able by this means to duplicate the discovery. Thus James Thomson, starting from the fact that ice floats on water, showed that it follows by mathe-

matics that ice can be melted and water prevented from freezing by pressure. This effect, which was at that time unknown, was afterwards verified by his brother, Lord Kelvin. Multitudes of similar duplication of physical discoveries by mathematics could be quoted.

I have been pleading in the interests of physics for a greater study of mathematics by physicists. I would also plead for a greater study of physics by mathematicians in the interest of pure mathematics.

The history of pure mathematics shows that many of the most important branches of the subject have arisen from the attempts made to get a mathematical solution of a problem suggested by physics. Thus the differential calculus arose from attempts to deal with the problem of moving bodies. Fourier's theorem resulted from attempts to deal with the vibrations of strings and the conduction of heat; indeed, it would seem that the most fruitful crop of scientific ideas is produced by cross-fertilisation between the mind and some definite fact, and that the mind by itself is comparatively unproductive.

I think, if we could trace the origin of some of our most comprehensive and important scientific ideas, it would be found that they arose in the attempt to find an explanation of some apparently trivial and very special phenomenon; when once started the ideas grew to such generality and importance that their modest origin could hardly be suspected. Water vapour we know will refuse to condense into rain unless there are particles of dust to form nuclei; so an idea before taking shape seems to require a nucleus of solid fact round which it can condense.

I have ventured to urge the closer union between mathematics and physics, because I think of late years there has been some tendency for these sciences to drift apart, and that the workers in applied mathematics are relatively fewer than they were some years ago. This is no doubt due to some extent to the remarkable developments made in the last few years in experimental physics on the one hand, and in the most abstract and metaphysical parts of pure mathematics on the other. The fascination of these has drawn workers to the frontiers of these regions who would otherwise have worked nearer the junction of the two. In part, too, it may be due to the fact that the problems with which the applied mathematician has to deal are exceedingly difficult, and many may have felt that the problems presented by the older physics have been worked over so often by men of the highest genius that there was but little chance of any problem which they could have any hope of solving being left.

But the newer developments of physics have opened virgin ground which has not yet been worked over, and which offers problems to the mathematician of great interest and novelty—problems which will suggest and require new methods of attack, the development of which will advance pure mathematics as well as physics.

I have alluded to the fact that pure mathematicians have been indebted to the study of concrete problems for the origination of some of their most valuable conceptions; and though no doubt pure mathematicians are in many ways very exceptional folk, yet in this respect they are very human. Most of us need to tackle some definite difficulty before our minds develop whatever powers they may possess. This is true for even the youngest of us, for our school boys and school girls, and I think the moral to be drawn from it is that we should aim at making the education in our schools as little bookish and as practical and concrete as possible.

I once had an illustration of the power of the concrete in stimulating the mind which made a very lasting impression upon me. One of my first pupils came to me with the assurance from his previous teacher that he knew little and cared less about mathematics, and that he had no chance of obtaining a degree in that subject. For some time I thought this estimate was correct, but he happened to be enthusiastic about billiards, and when we were reading that part of mechanics which deals with the collision of elastic bodies I pointed out that many of the

effects he was constantly observing were illustrations of the subject we were studying. From that time he was a changed man. He had never before regarded mathematics as anything but a means of annoying innocent undergraduates; now, when he saw what important results it could obtain, he became enthusiastic about it, developed very considerable mathematical ability, and, though he had already wasted two out of his three years at college, took a good place in the Mathematical Tripos.

It is possible to read books, to pass examinations without the higher qualities of the mind being called into play. Indeed, I doubt if there is any process in which the mind is more quiescent than in reading without interest. I might appeal to the widespread habit of reading in bed as a prevention of insomnia as a proof of this. But it is not possible for a boy to make a boat or for a girl to cook a dinner without using their brains. With practical things the difficulties have to be surmounted, the boat must be made watertight, the dinner must be cooked, while in reading there is always the hope that the difficulties which have been slurred over will not be set in the examination.

I think it was Helmholtz who said that often in the course of a research more thought and energy were spent in reducing a refractory piece of brass to order than in devising the method or planning the scheme of campaign. This constant need for thought and action gives to original research in any branch of experimental science great educational value even for those who will not become professional men of science. I have had considerable experience with students beginning research in experimental physics, and I have always been struck by the quite remarkable improvement in judgment, independence of thought, and maturity produced by a year's research. Research develops qualities which are apt to atrophy when the student is preparing for examinations, and, quite apart from the addition of new knowledge to our store, is of the greatest importance as a means of education.

It is the practice in many universities to make special provision for the reception of students from other universities who wish to do original research or to study the more advanced parts of their subject, and considerable numbers of such students migrate from one university to another. I think it would be a good thing if this practice were to extend to students at an earlier stage in their career; especially should I like to see a considerable interchange of students between the universities in the Mother Country and those in the Colonies.

I am quite sure that many of our English students, especially those destined for public life, could have no more valuable experience than to spend a year in one or other of your universities, and I hope some of your students might profit by a visit to ours.

I can think of nothing more likely to lead to a better understanding of the feelings, the sympathies, and, what is not less important, the prejudices, of one country by another, than by the youths of those countries spending a part of their student life together. Undergraduates as a rule do not wear a mask either of politeness or any other material, and have probably a better knowledge of each other's opinions and points of view—in fact, know each other better than do people of riper age. To bring this communion of students about there must be co-operation between the universities throughout the Empire; there must be recognition of each other's examinations, residence, and degrees. Before this can be accomplished there must, as my friend Mr. E. B. Sargent pointed out in a lecture given at the McGill University, be co-operation and recognition between the universities in each part of the Empire. I do not mean for a moment that all universities in a country should be under one government. I am a strong believer in the individuality of universities, but I do not think this is in any way inconsistent with the policy of an open door from one university to every other in the Empire.

It has usually been the practice of the President of this Association to give some account of the progress made in

the last few years in the branch of science which he has the honour to represent.

I propose this evening to follow that precedent and to attempt to give a very short account of some of the more recent developments of physics, and the new conceptions of physical processes to which they have led.

The period which has elapsed since the Association last met in Canada has been one of almost unparalleled activity in many branches of physics, and many new and unsuspected properties of matter and electricity have been discovered. The history of this period affords a remarkable illustration of the effect which may be produced by a single discovery; for it is, I think, to the discovery of the Röntgen rays that we owe the rapidity of the progress which has recently been made in physics. A striking discovery like that of the Röntgen rays acts much like the discovery of gold in a sparsely populated country; it attracts workers who come in the first place for the gold, but who may find that the country has other products, other charms, perhaps even more valuable than the gold itself. The country in which the gold was discovered in the case of the Röntgen rays was the department of physics dealing with the discharge of electricity through gases, a subject which, almost from the beginning of electrical science, had attracted a few enthusiastic workers, who felt convinced that the key to unlock the secret of electricity was to be found in a vacuum tube. Röntgen, in 1895, showed that when electricity passed through such a tube, the tube emitted rays which could pass through bodies opaque to ordinary light; which could, for example, pass through the flesh of the body and throw a shadow of the bones on a suitable screen. The fascination of this discovery attracted many workers to the subject of the discharge of electricity through gases, and led to great improvements in the instruments used in this type of research. It is not, however, to the power of probing dark places, important though this is, that the influence of Röntgen rays on the progress of science has mainly been due; it is rather because these rays make gases, and, indeed, solids and liquids, through which they pass conductors of electricity. It is true that before the discovery of these rays other methods of making gases conductors were known, but none of these was so convenient for the purposes of accurate measurement.

The study of gases exposed to Röntgen rays has revealed in such gases the presence of particles charged with electricity; some of these particles are charged with positive, others with negative electricity.

The properties of these particles have been investigated; we know the charge they carry, the speed with which they move under an electric force, the rate at which the oppositely charged ones re-combine, and these investigations have thrown a new light, not only on electricity, but also on the structure of matter.

We know from these investigations that electricity, like matter, is molecular in structure, that just as a quantity of hydrogen is a collection of an immense number of small particles called molecules, so a charge of electricity is made up of a great number of small charges, each of a perfectly definite and known amount.

Helmholtz said in 1880 that in his opinion the evidence in favour of the molecular constitution of electricity was even stronger than that in favour of the molecular constitution of matter. How much stronger is that evidence now, when we have measured the charge on the unit and found it to be the same from whatever source the electricity is obtained. Nay, further, the molecular theory of matter is indebted to the molecular theory of electricity for the most accurate determination of its fundamental quantity, the number of molecules in any given quantity of an elementary substance.

The great advantage of the electrical methods for the study of the properties of matter is due to the fact that whenever a particle is electrified it is very easily identified, whereas an uncharged molecule is most elusive; and it is only when these are present in immense numbers that we are able to detect them. A very simple calculation will

illustrate the difference in our power of detecting electrified and unelectrified molecules. The smallest quantity of unelectrified matter ever detected is probably that of neon, one of the inert gases of the atmosphere. Professor Strutt has shown that the amount of neon in one-twentieth of a cubic centimetre of the air at ordinary pressures can be detected by the spectroscope; Sir William Ramsay estimates that the neon in the air only amounts to one part of neon in 100,000 parts of air, so that the neon in one-twentieth of a cubic centimetre of air would only occupy at atmospheric pressure a volume of half a millionth of a cubic centimetre. When stated in this form the quantity seems exceedingly small, but in this small volume there are about ten million million molecules. Now the population of the earth is estimated at about fifteen hundred millions, so that the smallest number of molecules of neon we can identify is about 7000 times the population of the earth. In other words, if we had no better test for the existence of a man than we have for that of an unelectrified molecule we should come to the conclusion that the earth is uninhabited. Contrast this with our power of detecting electrified molecules. We can by the electrical method, even better by the cloud method of C. T. R. Wilson, detect the presence of three or four charged particles in a cubic centimetre. Rutherford has shown that we can detect the presence of a single α -particle. Now the particle is a charged atom of helium; if this atom had been uncharged we should have required more than a million million of them, instead of one, before we should have been able to detect them.

We may, I think, conclude, since electrified particles can be studied with so much greater ease than unelectrified ones, that we shall obtain a knowledge of the ultimate structure of electricity before we arrive at a corresponding degree of certainty with regard to the structure of matter.

We have already made considerable progress in the task of discovering what the structure of electricity is. We have known for some time that of one kind of electricity—the negative—and a very interesting one it is. We know that negative electricity is made up of units all of which are of the same kind; that these units are exceedingly small compared with even the smallest atom, for the mass of the unit is only $1/1700$ part of the mass of an atom of hydrogen; that its radius is only 10^{-13} centimetre, and that these units, "corpuscles" as they have been called, can be obtained from all substances. The size of these corpuscles is on an altogether different scale from that of atoms; the volume of a corpuscle bears to that of the atom about the same relation as that of a speck of dust to the volume of this room. Under suitable conditions they move at enormous speeds which approach in some instances the velocity of light.

The discovery of these corpuscles is an interesting example of the way nature responds to the demands made upon her by mathematicians. Some years before the discovery of corpuscles it had been shown by a mathematical investigation that the mass of a body must be increased by a charge of electricity. This increase, however, is greater for small bodies than for large ones, and even bodies as small as atoms are hopelessly too large to show any appreciable effect; thus the result seemed entirely academic. After a time corpuscles were discovered, and these are so much smaller than the atom that the increase in mass due to the charge becomes not merely appreciable, but so great that, as the experiments of Kaufmann and Bucherer have shown, the whole of the mass of the corpuscle arises from its charge.

We know a great deal about negative electricity; what do we know about positive electricity? Is positive electricity molecular in structure? Is it made up into units, each unit carrying a charge equal in magnitude though opposite in sign to that carried by a corpuscle? Does, or does not, this unit differ, in size and physical properties, very widely from the corpuscle? We know that by suitable processes we can get corpuscles out of any kind of matter, and that the corpuscles will be the same

from whatever source they may be derived. Is a similar thing true for positive electricity? Can we get, for example, a positive unit from oxygen of the same kind as that we get from hydrogen?

For my own part, I think the evidence is in favour of the view that we can, although the nature of the unit of positive electricity makes the proof much more difficult than for the negative unit.

In the first place we find that the positive particles—"canalstrahlen" is their technical name—discovered by our distinguished guest, Dr. Goldstein, which are found when an electric discharge passes through a highly rarefied gas, are, when the pressure is very low, the same, whatever may have been the gas in the vessel to begin with. If we pump out the gas until the pressure is too low to allow the discharge to pass, and then introduce a small quantity of gas and re-start the discharge, the positive particles are the same whatever kind of gas may have been introduced.

I have, for example, put into the exhausted vessel oxygen, argon, helium, the vapour of carbon tetrachloride, none of which contain hydrogen, and found the positive particles to be the same as when hydrogen was introduced.

Some experiments made lately by Wellisch, in the Cavendish Laboratory, strongly support the view that there is a definite unit of positive electricity independent of the gas from which it is derived; these experiments were on the velocity with which positive particles move through mixed gases. If we have a mixture of methyl-iodide and hydrogen exposed to Röntgen rays, the effect of the rays on the methyl-iodide is so much greater than on the hydrogen that, even when the mixture contains only a small percentage of methyl-iodide, practically all the electricity comes from this gas, and not from the hydrogen.

Now, if the positive particles were merely the residue left when a corpuscle had been abstracted from the methyl-iodide, these particles would have the dimensions of a molecule of methyl-iodide; this is very large and heavy, and would therefore move more slowly through the hydrogen molecules than the positive particles derived from hydrogen itself, which would, on this view, be of the size and weight of the light hydrogen molecules. Wellisch found that the velocities of both the positive and negative particles through the mixture were the same as the velocities through pure hydrogen, although in the one case the ions had originated from methyl-iodide and in the other from hydrogen; a similar result was obtained when carbon tetrachloride, or acicular methyl, was used instead of methyl-iodide. These and similar results lead to the conclusion that the atom of the different chemical elements contain definite units of positive as well as of negative electricity, and that the positive electricity, like the negative, is molecular in structure.

The investigations made on the unit of positive electricity show that it is of quite a different kind from the unit of negative, the mass of the negative unit is exceedingly small compared with any atom, the only positive units that up to the present have been detected are quite comparable in mass with the mass of an atom of hydrogen; in fact, they seem equal to it. This makes it more difficult to be certain that the unit of positive electricity has been isolated, for we have to be on our guard against its being a much smaller body attached to the hydrogen atoms which happen to be present in the vessel. If the positive units have a much greater mass than the negative ones, they ought not to be so easily deflected by magnetic forces when moving at equal speeds; and, in general, the insensibility of the positive particles to the influence of a magnet is very marked; though there are cases when the positive particles are much more readily deflected, and these have been interpreted as proving the existence of positive units comparable in mass with the negative ones. I have found, however, that in these cases the positive particles are moving very slowly, and that the ease with which they are deflected is due to the smallness of the velocity and not to that of the mass. It should, however, be noted

that M. Jean Becquerel has observed in the absorption spectra of some minerals, and Professor Wood in the rotation of the plane of polarisation by sodium vapour, effects which could be explained by the presence in the substances of positive units comparable in mass with corpuscles. This, however, is not the only explanation which can be given of these effects, and at present the smallest positive electrified particles of which we have direct experimental evidence have masses comparable with that of an atom of hydrogen.

A knowledge of the mass and size of the two units of electricity, the positive and the negative, would give us the material for constructing what may be called a molecular theory of electricity, and would be a starting-point for a theory of the structure of matter; for the most natural view to take, as a provisional hypothesis, is that matter is just a collection of positive and negative units of electricity, and that the forces which hold atoms and molecules together, the properties which differentiate one kind of matter from another, all have their origin in the electrical forces exerted by positive and negative units of electricity, grouped together in different ways in the atoms of the different elements.

As it would seem that the units of positive and negative electricity are of very different sizes, we must regard matter as a mixture containing systems of very different types, one type corresponding to the small corpuscle, the other to the large positive unit.

Since the energy associated with a given charge is greater the smaller the body on which the charge is concentrated, the energy stored up in the negative corpuscles will be far greater than that stored up by the positive. The amount of energy which is stored up in ordinary matter in the form of the electrostatic potential energy of its corpuscles is, I think, not generally realised. All substances give out corpuscles, so that we may assume that each atom of a substance contains at least one corpuscle. From the size and the charge on the corpuscle, both of which are known, we find that each corpuscle has 8×10^{-7} ergs of energy; this is on the supposition that the usual expressions for the energy of a charged body hold when, as in the case of a corpuscle, the charge is reduced to one unit. Now in one gm. of hydrogen there are about 6×10^{23} atoms, so if there is only one corpuscle in each atom the energy due to the corpuscles in a gm. of hydrogen would be 48×10^{16} ergs, or 11×10^9 calories. This is more than seven times the heat developed by one gm. of radium, or than that developed by the burning of five tons of coal. Thus we see that even ordinary matter contains enormous stores of energy; this energy is fortunately kept fast bound by the corpuscles; if at any time an appreciable fraction were to get free the earth would explode and become a gaseous nebula.

The matter of which I have been speaking so far is the material which builds up the earth, the sun, and the stars, the matter studied by the chemist, and which he can represent by a formula; this matter occupies, however, but an insignificant fraction of the universe, it forms but minute islands in the great ocean of the ether, the substance with which the whole universe is filled.

The ether is not a fantastic creation of the speculative philosopher; it is as essential to us as the air we breathe. For we must remember that we on this earth are not living on our own resources; we are dependent from minute to minute upon what we are getting from the sun, and the gifts of the sun are conveyed to us by the ether. It is to the sun that we owe not merely night and day, springtime and harvest, but it is the energy of the sun, stored up in coal, in waterfalls, in food, that practically does all the work of the world.

How great is the supply the sun lavishes upon us becomes clear when we consider that the heat received by the earth under a high sun and a clear sky is equivalent, according to the measurements of Langley, to about 7000 horse-power per acre. Though our engineers have not yet discovered how to utilise this enormous supply of

power, they will, I have not the slightest doubt, ultimately succeed in doing so; and when coal is exhausted and our water-power inadequate, it may be that this is the source from which we shall derive the energy necessary for the world's work. When that comes about, our centres of industrial activity may perhaps be transferred to the burning deserts of the Sahara, and the value of land determined by its suitability for the reception of traps to catch sunbeams.

This energy, in the interval between its departure from the sun and its arrival at the earth, must be in the space between them. Thus this space must contain something which, like ordinary matter, can store up energy, which can carry at an enormous pace the energy associated with light and heat, and which can, in addition, exert the enormous stresses necessary to keep the earth circling round the sun and the moon round the earth.

The study of this all-pervading substance is perhaps the most fascinating and important duty of the physicist.

On the electromagnetic theory of light, now universally accepted, the energy streaming to the earth travels through the ether in electric waves; thus practically the whole of the energy at our disposal has at one time or another been electrical energy. The ether must, then, be the seat of electrical and magnetic forces. We know, thanks to the genius of Clerk Maxwell, the founder and inspirer of modern electrical theory, the equations which express the relation between these forces, and although for some purposes these are all we require, yet they do not tell us very much about the nature of the ether.

The interest inspired by equations, too, in some minds is apt to be somewhat Platonic; and something more grossly mechanical—a model, for example, is felt by many to be more suggestive and manageable, and for them a more powerful instrument of research, than a purely analytical theory.

Is the ether dense or rare? Has it a structure? Is it at rest or in motion? are some of the questions which force themselves upon us.

Let us consider some of the facts known about the ether. When light falls on a body and is absorbed by it, the body is pushed forward in the direction in which the light is travelling, and if the body is free to move it is set in motion by the light. Now it is a fundamental principle of dynamics that when a body is set moving in a certain direction, or, to use the language of dynamics, acquires momentum in that direction, some other mass must lose the same amount of momentum; in other words, the amount of momentum in the universe is constant. Thus when the body is pushed forward by the light some other system must have lost the momentum the body acquires, and the only other system available is the wave of light falling on the body; hence we conclude that there must have been momentum in the wave in the direction in which it is travelling. Momentum, however, implies mass in motion. We conclude, then, that in the ether through which the wave is moving there is mass moving with the velocity of light. The experiments made on the pressure due to light enable us to calculate this mass, and we find that in a cubic kilometre of ether carrying light as intense as sunlight is at the surface of the earth, the mass moving is only about one-fifty-millionth of a milligram. We must be careful not to confuse this with the mass of a cubic kilometre of ether; it is only the mass moved when the light passes through it; the vast majority of the ether is left undisturbed by the light. Now, on the electro-magnetic theory of light, a wave of light may be regarded as made up of groups of lines of electric force moving with the velocity of light; and if we take this point of view we can prove that the mass of ether per cubic centimetre carried along is proportional to the energy possessed by these lines of electric force per cubic centimetre, divided by the square of the velocity of light. But though lines of electric force carry some of the ether along with them as they move, the amount so carried, even in the strongest electric fields we can produce, is but a minute fraction of the ether in their neighbourhood.

This is proved by an experiment made by Sir Oliver

Lodge in which light was made to travel through an electric field in rapid motion. If the electric field had carried the whole of the ether with it, the velocity of the light would have been increased by the velocity of the electric field. As a matter of fact no increase whatever could be detected, though it would have been registered if it had amounted to one-thousandth part of that of the field.

The ether carried along by a wave of light must be an exceedingly small part of the volume through which the wave is spread. Parts of this volume are in motion, but by far the greater part is at rest; thus in the wave front there cannot be uniformity, at some parts the ether is moving, at others it is at rest—in other words, the wave front must be more analogous to bright specks on a dark ground than to a uniformly illuminated surface.

The place where the density of the ether carried along by an electric field rises to its highest value is close to a corpuscle, for round the corpuscles are by far the strongest electric fields of which we have any knowledge. We know the mass of the corpuscle, we know from Kaufmann's experiments that this arises entirely from the electric charge, and is therefore due to the ether carried along with the corpuscle by the lines of force attached to it.

A simple calculation shows that one-half of this mass is contained in a volume seven times that of a corpuscle. Since we know the volume of the corpuscle as well as the mass, we can calculate the density of the ether attached to the corpuscle; doing so, we find it amounts to the prodigious value of about 5×10^{10} , or about 2000 million times that of lead. Sir Oliver Lodge, by somewhat different considerations, has arrived at a value of the same order of magnitude.

Thus around the corpuscle ether must have an extravagant density; whether the density is as great as this in other places depends upon whether the ether is compressible or not. If it is compressible, then it may be condensed round the corpuscles, and there have an abnormally great density; if it is not compressible, then the density in free space cannot be less than the number I have just mentioned.

With respect to this point we must remember that the forces acting on the ether close to the corpuscle are prodigious. If the ether were, for example, an ideal gas whose density increased in proportion to the pressure, however great the pressure might be, then if, when exposed to the pressures which exist in some directions close to the corpuscle, it had the density stated above, its density under atmospheric pressure would only be about 8×10^{-16} , or a cubic kilometre would have a mass less than a gm; so that instead of being almost incomparably denser than lead, it would be almost incomparably rarer than the lightest gas.

I do not know at present of any effect which would enable us to determine whether ether is compressible or not. And although at first sight the idea that we are immersed in a medium almost infinitely denser than lead might seem inconceivable, it is not so if we remember that in all probability matter is composed mainly of holes. We may, in fact, regard matter as possessing a bird-cage kind of structure in which the volume of the ether disturbed by the wires when the structure is moved is infinitesimal in comparison with the volume enclosed by them. If we do this, no difficulty arises from the great density of the ether; all we have to do is to increase the distance between the wires in proportion as we increase the density of the ether.

Let us now consider how much ether is carried along by ordinary matter, and what effects this might be expected to produce.

The simplest electrical system we know, an electrified sphere, has attached to it a mass of ether proportional to its potential energy, and such that if the mass were to move with the velocity of light its kinetic energy would equal the electrostatic potential energy of the particle. This result can be extended to any electrified system, and it can be shown that such a system binds a mass of the

ether proportional to its potential energy. Thus a part of the mass of any system is proportional to the potential energy of the system.

The question now arises, Does this part of the mass add anything to the weight of the body? If the ether were not subject to gravitational attraction it certainly would not; and even if the ether were ponderable, we might expect that as the mass is swimming in a sea of ether it would not increase the weight of the body to which it is attached. But if it does not, then a body with a large amount of potential energy may have an appreciable amount of its mass in a form which does not increase its weight, and thus the weight of a given mass of it may be less than that of an equal mass of some substance with a smaller amount of potential energy. Thus the weights of equal masses of these substances would be different. Now, experiments with pendulums, as Newton pointed out, enable us to determine with great accuracy the weights of equal masses of different substances. Newton himself made experiments of this kind, and found that the weights of equal masses were the same for all the materials he tried. Bessel, in 1830, made some experiments on this subject which are still the most accurate we possess, and he showed that the weights of equal masses of lead, silver, iron, brass did not differ by as much as one part in 60,000.

The substances tried by Newton and Bessel did not, however, include any of those substances which possess the marvellous power of radio-activity; the discovery of these came much later, and is one of the most striking achievements of modern physics.

These radio-active substances are constantly giving out large quantities of heat, presumably at the expense of their potential energy; thus when these substances reach their final non-radio-active state their potential energy must be less than when they were radio-active. Prof. Rutherford's measurements show that the energy emitted by one gm. of radium in the course of its degradation to non-radio-active forms is equal to the kinetic energy of a mass of one-thirteenth of a milligram moving with the velocity of light.

This energy, according to the rule I have stated, corresponds to a mass of one-thirteenth of a milligram of the ether, and thus a gm. of radium in its radio-active state must have at least one-thirteenth of a milligram more of ether attached to it than when it has been degraded into the non-radio-active forms. Thus if this ether does not increase the weight of the radium, the ratio of mass to weight for radium would be greater by about one part in 13,000 than for its non-radio-active products.

I attempted several years ago to find the ratio of mass to weight for radium by swinging a little pendulum, the bob of which was made of radium. I had only a small quantity of radium, and was not, therefore, able to attain any great accuracy. I found that the difference, if any, in the ratio of the mass to weight between radium and other substances was not more than one part in 2000. Lately we have been using at the Cavendish Laboratory a pendulum whose bob was filled with uranium oxide. We have got good reasons for supposing that uranium is a parent of radium, so that the great potential energy and large ethereal mass possessed by the radium will be also in the uranium; the experiments are not yet completed. It is, perhaps, expecting almost too much to hope that the radio-active substances may add to the great services they have already done to science by furnishing the first case in which there is some differentiation in the action of gravity.

The mass of ether bound by any system is such that if it were to move with the velocity of light its kinetic energy would be equal to the potential energy of the system. This result suggests a new view of the nature of potential energy. Potential energy is usually regarded as essentially different from kinetic energy. Potential energy depends on the configuration of the system, and can be calculated from it when we have the requisite data; kinetic energy, on the other hand, depends upon the velocity of the system. According to the principle of the conservation of energy the one form can be converted into the other at a

fixed rate of exchange, so that when one unit of one kind disappears a unit of the other simultaneously appears.

Now, in many cases this rule is all that we require to calculate the behaviour of the system, and the conception of potential energy is of the utmost value in making the knowledge derived from experiment and observation available for mathematical calculation. It must, however, I think, be admitted that from the purely philosophical point of view it is open to serious objection. It violates, for example, the principle of continuity. When a thing changes from a state A to a different state B, the principle of continuity requires that it must pass through a number of states intermediate between A and B, so that the transition is made gradually, and not abruptly. Now, when kinetic energy changes into potential, although there is no discontinuity in the quantity of the energy, there is in its quality, for we do not recognise any kind of energy intermediate between that due to the motion and that due to the position of the system, and some portions of energy are supposed to change *per saltum* from the kinetic to the potential form. In the case of the transition of kinetic energy into heat energy in a gas, the discontinuity has disappeared with a fuller knowledge of what the heat energy in a gas is due to. When we were ignorant of the nature of this energy, the transition from kinetic to thermal energy seemed discontinuous; but now we know that this energy is the kinetic energy of the molecules of which the gas is composed, so that there is no change in the type of energy when the kinetic energy of visible motion is transformed into the thermal energy of a gas—it is just the transference of kinetic energy from one body to another.

If we regard potential energy as the kinetic energy of portions of the ether attached to the system, then all energy is kinetic energy, due to the motion of matter or of portions of ether attached to the matter. I showed, many years ago, in my "Applications of Dynamics to Physics and Chemistry," that we could imitate the effects of the potential energy of a system by means of the kinetic energy of invisible systems connected in an appropriate manner with the main system, and that the potential energy of the visible universe may in reality be the kinetic energy of an invisible one connected up with it. We naturally suppose that this invisible universe is the luminiferous ether, that portions of the ether in rapid motion are connected with the visible systems, and that their kinetic energy is the potential energy of the systems.

We may thus regard the ether as a bank in which we may deposit energy and withdraw it at our convenience. The mass of the ether attached to the system will change as the potential energy changes, and thus the mass of a system whose potential energy is changing cannot be constant; the fluctuations in mass under ordinary conditions are, however, so small that they cannot be detected by any means at present at our disposal. Inasmuch as the various forms of potential energy are continually being changed into heat energy, which is the kinetic energy of the molecules of matter, there is a constant tendency for the mass of a system such as the earth or the sun to diminish, and thus as time goes on for the mass of ether gripped by the material universe to become smaller and smaller; the rate at which it would diminish would, however, get slower as time went on, and there is no reason to think that it would ever get below a very large value.

Radiation of light and heat from an incandescent body like the sun involves a constant loss of mass by the body. Each unit of energy radiated carries off its quota of mass, but as the mass ejected from the sun per year is only one part in 20 billionths (1 in 2×10^{13}) of the mass of the sun, and as this diminution in mass is not necessarily accompanied by any decrease in its gravitational attraction, we cannot expect to be able to get any evidence of this effect.

As our knowledge of the properties of light has progressed, we have been driven to recognise that the ether, when transmitting light, possesses properties which, before the introduction of the electro-magnetic theory, would have

been thought to be peculiar to an emission theory of light and to be fatal to the theory that light consists of undulations.

Take, for example, the pressure exerted by light. This would follow as a matter of course if we supposed light to be small particles moving with great velocities, for these, if they struck against a body, would manifestly tend to push it forward, while on the undulatory theory there seemed no reason why any effect of this kind should take place.

Indeed, in 1792, this very point was regarded as a test between the theories, and Bennet made experiments to see whether or not he could find any traces of this pressure. We now know that the pressure is there, and if Bennet's instrument had been more sensitive he must have observed it. It is perhaps fortunate that Bennet had not at his command more delicate apparatus. Had he discovered the pressure of light, it would have shaken confidence in the undulatory theory and checked that magnificent work at the beginning of the last century which so greatly increased our knowledge of optics.

As another example, take the question of the distribution of energy in a wave of light. On the emission theory the energy in the light is the kinetic energy of the light particles. Thus the energy of light is made up of distinct units, the unit being the energy of one of the particles.

The idea that the energy has a structure of this kind has lately received a good deal of support. Planck, in a very remarkable series of investigations on the Thermodynamics of Radiation, pointed out that the expressions for the energy and entropy of radiant energy were of such a form as to suggest that the energy of radiation, like that of a gas on the molecular theory, was made up of distinct units, the magnitude of the unit depending on the colour of the light; and on this assumption he was able to calculate the value of the unit, and from this deduce incidentally the value of Avogadro's constant—the number of molecules in a cubic centimetre of gas at standard temperature and pressure.

This result is most interesting and important because if it were a legitimate deduction from the Second Law of Thermodynamics, it would appear that only a particular type of mechanism for the vibrators which give out light and the absorbers which absorb it could be in accordance with that law.

If this were so, then, regarding the universe as a collection of machines all obeying the laws of dynamics, the Second Law of Thermodynamics would only be true for a particular kind of machine.

There seems, however, grave objection to this view, which I may illustrate by the case of the First Law of Thermodynamics, the principle of the Conservation of Energy. This must be true whatever be the nature of the machines which make up the universe, provided they obey the laws of dynamics, any application of the principle of the Conservation of Energy could not discriminate between one type of machine and another.

Now, the Second Law of Thermodynamics, though not a dynamical principle in as strict a sense as the law of the Conservation of Energy, is one that we should expect to hold for a collection of a large number of machines of any type, provided that we could not directly affect the individual machines, but could only observe the average effects produced by an enormous number of them. On this view, the Second Law, as well as the First, should be incapable of saying that the machines were of any particular type; so that investigations founded on thermodynamics, though the expressions they lead to may suggest—cannot, I think, be regarded as proving—the unit structure of light energy.

It would seem as if in the application of thermodynamics to radiation some additional assumption has been implicitly introduced, for these applications lead to definite relations between the energy of the light of any particular wavelength and the temperature of the luminous body.

Now, a possible way of accounting for the light emitted by hot bodies is to suppose that it arises from the collisions

of corpuscles with the molecules of the hot body, but it is only for one particular law of force between the corpuscles and the molecules that the distribution of energy would be the same as that deduced by the Second Law of Thermodynamics, so that in this case, as in the other, the results obtained by the application of thermodynamics to radiation would require us to suppose that the Second Law of Thermodynamics is only true for radiation when the radiation is produced by mechanism of a special type.

Quite apart, however, from considerations of thermodynamics, we should expect that the light from a luminous source should in many cases consist of parcels, possessing, at any rate to begin with, a definite amount of energy. Consider, for example, the case of a gas like sodium vapour, emitting light of a definite wave-length; we may imagine that this light, consisting of electrical waves, is emitted by systems resembling Leyden jars. The energy originally possessed by such a system will be the electrostatic energy of the charged jar. When the vibrations are started, this energy will be radiated away into space, the radiation forming a complex system, containing, if the jar has no electrical resistance, the energy stored up in the jar.

The amount of this energy will depend on the size of the jar and the quantity of electricity with which it is charged. With regard to the charge, we must remember that we are dealing with systems formed out of single molecules, so that the charge will only consist of one or two natural units of electricity, or, at all events, some small multiple of that unit, while for geometrically similar Leyden jars the energy for a given charge will be proportional to the frequency of the vibration; thus, the energy in the bundle of radiation will be proportional to the frequency of the vibration.

We may picture to ourselves the radiation as consisting of the lines of electric force which, before the vibrations were started, were held, bound by the charges on the jar, and which, when the vibrations begin, are thrown into rhythmic undulations, liberated from the jar and travel through space with the velocity of light.

Now let us suppose that this system strikes against an uncharged condenser and gives it a charge of electricity, the charge on the plates of the condenser must be at least one unit of electricity, because fractions of this charge do not exist, and each unit charge will anchor a unit tube of force, which must come from the parcel of radiation falling upon it. Thus a tube in the incident light will be anchored by the condenser, and the parcel formed by this tube will be anchored and withdrawn as a whole from the pencil of light incident on the condenser. If the energy required to charge up the condenser with a unit of electricity is greater than the energy in the incident parcel, the tube will not be anchored, and the light will pass over the condenser and escape from it. These principles that radiation is made up of units, and that it requires a unit possessing a definite amount of energy to excite radiation in a body on which it falls, perhaps receive their best illustration in the remarkable laws governing Secondary Röntgen radiation, recently discovered by Professor Barkla. Professor Barkla has found that each of the different chemical elements, when exposed to Röntgen rays, emit a definite type of secondary radiation whatever may have been the type of primary, thus lead emits one type, copper another, and so on; but these radiations are not excited at all if the primary radiation is of a softer type than the specific radiation emitted by the substance; thus the secondary radiation from lead being harder than that from copper; if copper is exposed to the secondary radiation from lead the copper will radiate, but lead will not radiate when exposed to copper. Thus, if we suppose that the energy in a unit of hard Röntgen rays is greater than that in one of soft, Barkla's results are strikingly analogous to those which would follow on the unit theory of light.

Though we have, I think, strong reasons for thinking that the energy in the light waves of definite wave-length is done up into bundles, and that these bundles, when emitted, all possess the same amount of energy, I do not

think there is any reason for supposing that in any casual specimen of light of this wave-length, which may subsequent to its emission have been many times refracted or reflected, the bundles possess any definite amount of energy. For consider what must happen when a bundle is incident on a surface such as glass, when part of it is reflected and part transmitted. The bundle is divided into two portions, in each of which the energy is less than the incident bundle, and since these portions diverge and may ultimately be many thousands of miles apart, it would seem meaningless to still regard them as forming one unit. Thus the energy in the bundles of light, after they have suffered partial reflection, will not be the same as in the bundles when they were emitted. The study of the dimensions of these bundles, for example, the angle they subtend at the luminous source, is an interesting subject for investigation; experiments on interference between rays of light emerging in different directions from the luminous source would probably throw light on this point.

I now pass to a very brief consideration of one of the most important and interesting advances ever made in physics, and in which Canada, as the place of the labours of Professors Rutherford and Soddy, has taken a conspicuous part. I mean the discovery and investigation of radio-activity. Radio-activity was brought to light by the Röntgen rays. One of the many remarkable properties of these rays is to excite phosphorescence in certain substances, including the salts of uranium, when they fall upon them. Since Röntgen rays produce phosphorescence, it occurred to Becquerel to try whether phosphorescence would produce Röntgen rays. He took some uranium salts which had been made to phosphoresce by exposure not to Röntgen rays but to sunlight, tested them, and found that they gave out rays possessing properties similar to Röntgen rays. Further investigation showed, however, that to get these rays it was not necessary to make the uranium phosphoresce, that the salts were just as active if they had been kept in the dark. It thus appeared that the property was due to the metal and not to the phosphorescence, and that uranium and its compounds possessed the power of giving out rays which, like Röntgen rays, affect a photographic plate, make certain minerals phosphoresce, and make gases through which they pass conductors of electricity.

Niepe de Saint-Victor had observed some years before this discovery that paper soaked in a solution of uranium nitrate affected a photographic plate, but the observation excited but little interest. The ground had not been prepared, by the discovery of the Röntgen rays, for its reception, and it withered and was soon forgotten.

Shortly after Becquerel's discovery of uranium, Schmidt found that thorium possessed similar properties. Then Monsieur and Madame Curie, after a most difficult and laborious investigation, discovered two new substances, radium and polonium, possessing this property to an enormously greater extent than either thorium or uranium, and this was followed by the discovery of actinium by Debierne. Now the researches of Rutherford and others have led to the discovery of so many new radio-active substances that any attempt at christening seems to have been abandoned, and they are denoted, like policemen, by the letters of the alphabet.

Mr. Campbell has recently found that potassium, though far inferior in this respect to any of the substances I have named, emits an appreciable amount of radiation, the amount depending only on the quantity of potassium, and being the same whatever the source from which the potassium is obtained or whatever the elements with which it may be in combination.

The radiation emitted by these substances is of three types known as α -, β -, and γ -rays. The α -rays have been shown by Rutherford to be positively electrified atoms of helium, moving with speeds which reach up to about one-tenth of the velocity of light. The β -rays are negatively electrified corpuscles, moving in some cases with very nearly the velocity of light itself, while the γ -rays are unelectrified, and are analogous to the Röntgen rays.

The radio-activity of uranium was shown by Crookes to arise from something mixed with the uranium, and which differed sufficiently in properties from the uranium itself to enable it to be separated by chemical analysis. He took some uranium, and by chemical treatment separated it into two portions, one of which was radio-active and the other not.

Next, Becquerel found that if these two portions were kept for several months, the part which was not radio-active to begin with regained radio-activity, while the part which was radio-active to begin with had lost its radio-activity. These effects and many others receive a complete explanation by the theory of radio-active change which we owe to Rutherford and Soddy.

According to this theory, the radio-active elements are not permanent, but are gradually breaking up into elements of lower atomic weight; uranium, for example, is slowly breaking up, one of the products being radium, while radium breaks up into a radio-active gas called radium emanation, the emanation into another radio-active substance, and so on, and that the radiations are a kind of swan's song emitted by the atoms when they pass from one form to another; that, for example, it is when a radium atom breaks up and an atom of the emanation appears that the rays which constitute the radio-activity are produced.

Thus, on this view the atoms of the radio-active elements are not immortal, they perish after a life whose average value ranges from thousands of millions of years in the case of uranium to a second or so in the case of the gaseous emanation from actinium.

When the atoms pass from one state to another they give out large stores of energy, thus their descendants do not inherit the whole of their wealth of stored-up energy, the estate becomes less and less wealthy with each generation; we find, in fact, that the politician, when he imposes death duties, is but imitating a process which has been going on for ages in the case of these radio-active substances.

Many points of interest arise when we consider the rate at which the atoms of radio-active substance disappear. Rutherford has shown that whatever be the age of these atoms, the percentage of atoms which disappear in one second is always the same; another way of putting it is that the expectation of life of an atom is independent of its age—that an atom of radium one thousand years old is just as likely to live for another thousand years as one just sprung into existence.

Now this would be the case if the death of the atom were due to something from outside which struck old and young indiscriminately; in a battle, for example, the chance of being shot is the same for old and young; so that we are inclined at first to look to something coming from outside as the cause why an atom of radium, for example, suddenly changes into an atom of the emanation. But here we are met with the difficulty that no changes in the external conditions that we have as yet been able to produce have had any effect on the life of the atom; as far as we know at present the life of a radium atom is the same at the temperature of a furnace as at that of liquid air—it is not altered by surrounding the radium by thick screens of lead or other dense materials to ward off radiation from outside, and what to my mind is especially significant, it is the same when the radium is in the most concentrated form, when its atoms are exposed to the vigorous bombardment from the rays given off by the neighbouring atoms, as when it is in the most dilute solution, when the rays are absorbed by the water which separates one atom from another. This last result seems to me to make it somewhat improbable that we shall be able to split up the atoms of the non-radio-active elements by exposing them to the radiation from radium; if this radiation is unable to affect the unstable radio-active atoms, it is somewhat unlikely that it will be able to affect the much more stable non-radio-active elements.

The evidence we have at present is against a disturbance

coming from outside breaking up of the radio-active atoms, and we must therefore look to some process of decay in the atom itself; but if this is the case, how are we to reconcile it with the fact that the expectation of life of an atom does not diminish as the atom gets older? We can do this if we suppose that the atoms when they are first produced have not all the same strength of constitution, that some are more robust than others, perhaps because they contain more intrinsic energy to begin with, and will therefore have a longer life. Now if when the atoms are first produced there are some which will live for one year, some for ten, some for a thousand, and so on; and if lives of all durations, from nothing to infinity, are present in such proportion that the number of atoms which will live longer than a certain number of years decrease in a constant proportion for each additional year of life, we can easily prove that the expectation of life of an atom will be the same whatever its age may be. On this view the different atoms of a radio-active substance are not, in all respects, identical.

The energy developed by radio-active substances is exceedingly large, one grm. of radium developing nearly as much energy as would be produced by burning a ton of coal. This energy is mainly in the α particles, the positively charged helium atoms which are emitted when the change in the atom takes place; if this energy were produced by electrical forces it would indicate that the helium atom had moved through a potential difference of about two million volts on its way out of the atom of radium. The source of this energy is a problem of the deepest interest; if it arises from the repulsion of similarly electrified systems exerting forces varying inversely as the square of the distance, then to get the requisite amount of energy the systems, if their charges were comparable with the charge on the α particle, could not when they start be further apart than the radius of a corpuscle, 10^{-13} cm. If we suppose that the particles do not acquire this energy at the explosion, but that before they are shot out of the radium atom they move in circles inside this atom with the speed with which they emerge, the forces required to prevent particles moving with this velocity from flying off at a tangent are so great that finite charges of electricity could only produce them at distances comparable with the radius of a corpuscle.

One method by which the requisite amount of energy could be obtained is suggested by the view to which I have already alluded—that in the atom we have electrified systems of very different types, one small, the other large; the radius of one type is comparable with 10^{-13} cm., that of the other is about 100,000 times greater. The electrostatic potential energy in the smaller bodies is enormously greater than that in the larger ones; if one of these small bodies were to explode and expand to the size of the larger ones, we should have a liberation of energy large enough to endow an α particle with the energy it possesses. Is it possible that the positive units of electricity were, to begin with, quite as small as the negative, but while in the course of ages most of these have passed from the smaller stage to the larger, there are some small ones still lingering in radio-active substances, and it is the explosion of these which liberates the energy set free during radio-active transformation?

The properties of radium have consequences of enormous importance to the geologist as well as to the physicist or chemist. In fact, the discovery of these properties has entirely altered the aspect of one of the most interesting geological problems, that of the age of the earth. Before the discovery of radium it was supposed that the supplies of heat furnished by chemical changes going on in the earth were quite insignificant, and that there was nothing to replace the heat which flows from the hot interior of the earth to the colder crust. Now when the earth first solidified it only possessed a certain amount of capital in the form of heat, and if it is continually spending this capital and not gaining any fresh heat it is evident that the process cannot have been going on for more than a

certain number of years, otherwise the earth would be colder than it is. Lord Kelvin in this way estimated the age of the earth to be less than 100 million years. Though the quantity of radium in the earth is an exceedingly small fraction of the mass of the earth, only amounting, according to the determinations of Professors Strutt and Joly, to about five grms. in a cube whose side is 100 miles, yet the amount of heat given out by this small quantity of radium is so great that it is more than enough to replace the heat which flows from the inside to the outside of the earth. This, as Rutherford has pointed out, entirely vitiates the previous method of determining the age of the earth. The fact is that the radium gives out so much heat that we do not quite know what to do with it, for if there was as much radium throughout the interior of the earth as there is in its crust, the temperature of the earth would increase much more rapidly than it does as we descend below the earth's surface. Prof. Strutt has shown that if radium behaves in the interior of the earth as it does at the surface, rocks similar to those in the earth's crust cannot extend to a depth of more than forty-five miles below the surface.

It is remarkable that Prof. Milne from the study of earthquake phenomena had previously come to the conclusion that rocks similar to those at the earth's surface only descend a short distance below the surface; he estimates this distance at about thirty miles, and concludes that at a depth greater than this the earth is fairly homogeneous.

Though the discovery of radio-activity has taken away one method of calculating the age of the earth it has supplied another.

The gas helium is given out by radio-active bodies, and since, except in beryls, it is not found in minerals which do not contain radio-active elements, it is probable that all the helium in these minerals has come from these elements. In the case of a mineral containing uranium, the parent of radium in radio-active equilibrium, with radium and its products, helium will be produced at a definite rate. Helium, however, unlike the radio-active elements, is permanent and accumulates in the mineral; hence if we measure the amount of helium in a sample of rock and the amount produced by the sample in one year we can find the length of time the helium has been accumulating, and hence the age of the rock. This method, which is due to Prof. Strutt, may lead to determinations not merely of the average age of the crust of the earth, but of the ages of particular rocks and the date at which the various strata were deposited; he has, for example, shown in this way that a specimen of the mineral thorianite must be more than 240 million years old.

The physiological and medical properties of the rays emitted by radium is a field of research in which enough has already been done to justify the hope that it may lead to considerable alleviation of human suffering. It seems quite definitely established that for some diseases, notably rodent ulcer, treatment with these rays has produced remarkable cures; it is imperative, lest we should be passing over a means of saving life and health, that the subject should be investigated in a much more systematic and extensive manner than there has yet been either time or material for. Radium is, however, so costly that few hospitals could afford to undertake pioneering work of this kind; fortunately, however, through the generosity of Sir Ernest Cassel and Lord Iveagh, a Radium Institute, under the patronage of his Majesty the King, has been founded in London for the study of the medical properties of radium, and for the treatment of patients suffering from diseases for which radium is beneficial.

The new discoveries made in physics in the last few years, and the ideas and potentialities suggested by them, have had an effect upon the workers in that subject akin to that produced in literature by the Renaissance. Enthusiasm has been quickened, and there is a hopeful, youthful, perhaps exuberant, spirit abroad which leads men to make with confidence experiments which would have been thought fantastic twenty years ago. It has quite dispelled the pessimistic feeling, not uncommon at that time, that

all the interesting things had been discovered, and all that was left was to alter a decimal or two in some physical constant. There was never any justification for this feeling, there never were any signs of an approach to finality in science. The sum of knowledge is at present, at any rate, a diverging not a converging series. As we conquer peak after peak we see in front of us regions full of interest and beauty, but we do not see our goal, we do not see the horizon; in the distance tower still higher peaks, which will yield to those who ascend them still wider prospects, and deepen the feeling, whose truth is emphasised by every advance in science, that "Great are the Works of the Lord."

NOTICES OF BOOKS.

Welding and Cutting Metals by Aid of Gases or Electricity. By Dr. L. A. GROTH. London: Archibald Constable and Co., Ltd. 1909.

IN this book many erroneous ideas on the subject of the cost and difficulty of welding by electricity and by compressed gases are corrected, and the merits of the different processes are carefully weighed. Methods of preparing the gases which can be used in autogenous welding are discussed, and their properties are described. Special stress is laid upon the need for skill and care in using the gases, especially acetylene, with which accidents have been frequent, and the author has drawn up impartial comparisons of the advantages and disadvantages of the different gases. The reports by engineers of the results obtained with the processes are convincing, and the author does valuable work in pointing out the need for the further investigation of many disputed questions, especially those relating to the nature of the action of the compressed gases upon the metals.

CORRESPONDENCE.

THE JAPAN - BRITISH EXHIBITION, 1910.

To the Editor of the Chemical News.

SIR,—Under the auspices of the Imperial Government of Japan and with the cordial approval of the British Government, arrangements have been completed for a great Japan-British Exhibition to be held next year at the White City, Shepherd's Bush. In view of the alliance between Great Britain and Japan no conjunction could be happier. His Majesty the King, with characteristic solicitude for everything that makes for the extension of British Trade and with keen appreciation of our Allies in the Far East, sent to Prince Arthur of Connaught, the Chairman at the Inaugural Banquet of the Exhibition, the following message:—

"I understand you will preside this evening at a dinner given in connection with the proposed Anglo-Japanese Exhibition next year. International Exhibitions in these days largely depend on private support, and I hope therefore that the Japanese and British people will come forward to promote an undertaking which has for its object an increase in the commercial prosperity of both countries, and the uniting still closer of the bonds of fellowship which already exist between them."

His Imperial Majesty, the Emperor of Japan, also sent a telegram as follows:—

"I take advantage of the occasion to tender my congratulations to your Royal Highness and to those who join you in celebrating the inception of the 'Anglo-Japanese Exhibition,' and to express my sincere wishes for the complete success of the undertaking."

His Excellency the Japanese Ambassador on this occasion said that he felt confident that the Exhibition would confirm the friendly sentiments and would greatly help the commercial relations between the two countries, and spoke of the intense interest taken in the Exhibition by the people of Japan, and of the large sum of money voted for it by the Imperial Diet.

The Lord Mayor of London pledged his official and personal support, and expressed the conviction that nowhere would more real interest be taken in the Exhibition than in the Ancient City of London. The full support of the London Chamber of Commerce and of the Associated Chambers of Commerce of the United Kingdom is also assured.

As Hon. President and President of the Exhibition, we venture to ask the courtesy of your space in order to invite universal support for this specially important demonstration. The value of the traditional Art of Japan and the influence it has exercised on the Fine and Industrial Arts of the World cannot be over-estimated, and on the occasion of this Exhibition the nobles of Japan will pour out, from the treasures they have accumulated for centuries, Works of Art never before seen in this country and only by a favoured few in Japan.

The Committee joins us in appealing to possessors of the treasures of British Art to make a like revelation of those priceless works, many of which are but little known to the General Public, so as to equal, and if possible eclipse the magnificent display of Art at the Franco-British Exhibition.

The unique character of the Exhibition is sure to attract multitudes of people, not only from Japan and the United Kingdom, and the Colonies, and Dependencies, but from every European country, and from America, and cannot fail to increase the commerce of the two nations and to create new commercial channels between them and the rest of the world.

We therefore trust that the Manufacturers and Producers of this country, as well as those of the rest of the British Empire, will rise to the occasion by displaying the best of their respective productions in Arts and Industries, so as to make a representation worthy of this great opportunity.

The Exhibition will have the advantage of the beautiful buildings, already known to millions of people, which made the White City so famous in connection with the Franco-British Exhibition, and it only remains for the British Empire to provide a collection of exhibits which will worthily compare with those already promised by Japan, and to translate into reality the hope expressed by his Majesty the King that increased commercial prosperity and closer bonds of fellowship will result.—We have the honour to be, Sir,

ARTHUR, Hon. President, Japan-British Exhibition.
NORFOLK, President.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xlii., No. 10, 1909.

Researches on Rhodium.—A. Gubier and L. v. Müller.—The authors have found that the reduction of rhodium compounds to metal by means of hydrazine hydrate can be used for gravimetric analysis. By working with solutions which are not too concentrated the metal is separated, not as a black amorphous powder but in the form of glittering metallic scales. The derivatives used for the analyses were chloropentamminrhodium chloride, $\text{Rh}(\text{NH}_3)_5\text{Cl}_3$, and the corresponding bromide, $\text{Rh}(\text{NH}_3)_5\text{Br}_3$.

Benzaldehyde Ammonia.—Francis Francis.—When ammonia acts at a low temperature on a concentrated solution of benzaldehyde in a mixture of alcohol and water, a crystalline addition product of composition $(\text{C}_6\text{H}_5\cdot\text{CHO})_2\text{NH}_3$ separates. This "benzaldehyde ammonia" is *aa'*-dioxo-dibenzylamine, and is very unstable, rapidly giving hydrobenzamide, water, and benzaldehyde, $2\text{C}_6\text{H}_5\cdot\text{CH}(\text{OH})\cdot\text{NH}\cdot\text{CH}(\text{OH})\cdot\text{C}_6\text{H}_5 = (\text{C}_6\text{H}_5\cdot\text{CH}_2)_3\text{N}_2 + \text{C}_6\text{H}_5\cdot\text{CHO} + 3\text{H}_2\text{O}$.

p-Tolylaldehyde behaves similarly, giving the corresponding compound $\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OH})\cdot\text{NH}\cdot\text{CH}(\text{OH})\cdot\text{C}_6\text{H}_4\cdot\text{CH}_3$.

Formation of Ozone by Ultra-violet Light.—Franz Fischer.—Bordier and Nogier (*Comptes Rendus*, 1908, p. 354) have stated that ozone is not formed by the ultra-violet light of a quartz lamp, and they say that the smell observed in the neighbourhood of a burning quartz mercury lamp is not due to ozone, but to the effect of free electric discharges upon the olfactory nerves. The author has, however, actually condensed the ozone by means of liquid air, and has identified it by the violet coloration it produces on tetramethyl base papers as well as by its characteristic smell. He has also determined it quantitatively by leading it through potassium iodide solution and then titrating.

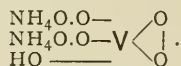
Genetic and Constitutive Relations in the Magnetic Properties of Ferrites and Iron Oxides.—Siegfried Hilpert.—From an exhaustive study of the magnetic properties of ferrites and iron oxides, the author concludes that in the series of the ferromagnetic iron oxide compounds the chemical cause of the appearance of magnetic properties depends only on the acid function of the iron oxide. Conversely, however, the acid character of the iron oxide does not in all cases produce ferromagnetic properties. Feebly magnetic ferrites must be heated to high temperatures before they exhibit magnetic properties. In the case of all the ferrites investigated it was possible to produce a magnetic modification. Moreover, all ferrites have the property which is common to the ferromagnetic metals of possessing transition temperatures above which the magnetic properties entirely disappear. These changes are generally reversible. The change of black ferrous-ferrous oxide into red iron oxide occurs without appreciable change in the magnetic properties, and apparently in this case there is no connection between the absorption of light and also the electrical conductivity and the magnetic properties.

Plumboniobite.—Otto Hauser and L. Finckh.—The authors have obtained a specimen of a mineral which apparently belongs to the samarskite-yttrotantalite series. On analysis it was found to contain 46 per cent Nb_2O_5 , 13 per cent UO_2 , 15 per cent Y_2O_3 , 8 per cent PbO , and 6 per cent FeO , besides small quantities of Ta, Ti, Zr, Th, &c. It appears to be a pyroniobate, and its formula may be $\left\{ \begin{array}{l} \text{R}_2^{\text{II}}\text{Nb}_2\text{O}_7 \\ \text{R}_1^{\text{III}}(\text{Nb}_2\text{O}_7)_3 \end{array} \right\}$; where $\text{R}^{\text{II}} = \text{Fe, Pb, Ca, UO}$, and $\text{R}^{\text{III}} = \text{Y, Yb, Gd, Al}$.

Lead Phosphates.—H. Alders and A. Stähler.—Tertiary lead phosphate, $\text{Pb}_3(\text{PO}_4)_2$, prepared by the action of excess of alkali phosphate on a soluble lead salt always contains alkali which cannot be removed by boiling with water. In order to get the pure tertiary salt, excess of lead acetate must be boiled with a little sodium phosphate, or the secondary salt must be boiled for a long time with water, when it is converted into the tertiary phosphate. Secondary lead phosphate, PbHPO_4 , can be very easily prepared by adding hot dilute phosphoric acid (about 25 per cent H_3PO_4) to boiling dilute lead nitrate solution. It then forms in fine crystals which can be re-crystallised in dilute phosphoric acid. Primary lead phosphate can be prepared by the action of excess of hot strong phosphoric acid on the secondary salt. The limits of stability of the secondary phosphate are the widest. The tertiary phosphate only exists when very little H_3PO_4 is present, and the primary when the H_3PO_4 concentration is very great.

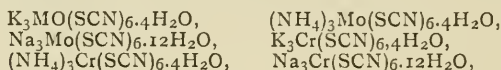
The latter changes very readily into the secondary phosphate when small changes of concentration occur.

Orthopervanadates.—P. Melikoff and E. Jelchchaninoff. —The ammonium salt of pervanadic acid, $(\text{NH}_4)_3\text{VO}_6 + 2\frac{1}{2}\text{H}_2\text{O}$, can be prepared by dissolving ammonium vanadate in concentrated ammonia solution, adding hydrogen peroxide to the cooled solution, and then treating the blue liquid thus obtained with alcohol. An ammoniacal solution of this salt, when treated with a large excess of H_2O_2 , yields a substance which is not a single compound but contains a salt richer in oxygen, of formula—



The potassium salt of pervanadic acid, $\text{K}_3\text{VO}_6 + 2\frac{1}{2}\text{H}_2\text{O}$, can be prepared similarly, starting with the potassium salt of metavanadium or pyropervanadium acid. These results show that while the salts of orthoptertantallic acid are formed in dilute solution and in presence of a slight excess of hydrogen peroxide and alkali, the analogous compounds of pervanadic acid are obtained only from concentrated solutions, and with a large excess of H_2O_2 and alkali.

Hexarhodanate Salts of Molybdenum.—Arthur Rosenheim.—The crystallographic investigation of the six salts,—



shows that the salts of the same series, *i.e.*, the molybdenum or chromium compounds, are not isomorphous, but that, on the other hand, the analogous molybdenum and chromium salts are isomorphous, the potassium salts crystallising in the pseudohexagonal system, the ammonium salts in the rhombic system, and the sodium salts asymmetrically. These results appear to confirm the formula $\text{K}_3\text{Mo}(\text{SCN})_6 \cdot 4\text{H}_2\text{O}$ for the molybdenum hexarhodanides. The measurements also show that, in spite of the complete analogy in the composition of the salts of the chromium series, there is no isomorphism between the potassium and the ammonium salt.

MISCELLANEOUS.

Prizes for the Solution of Technical Problems.—The Council of the Society of Dyers and Colourists have pleasure in offering prizes for the solution of the technical problems specified below. It is hoped that it will be possible to gradually develop a comprehensive prize scheme which will prove of value to the progress of the dyeing and allied industries, and will stimulate research. The Council request the assistance and co-operation of members and others in developing this scheme, and will be glad to receive additional offers of prizes and problems. The following is a list of problems and prizes:—

The Silver or Bronze Medal of the Society and £20 for a full investigation of the mordanting properties of various tannin materials, more especially—(a) As to the relative affinity for cotton of the tannins of galls, myrabolams, sumach, dividivi, &c. (b) As to the relative fastness of the colour lakes produced with these tannins and basic colours, in conjunction with antimony, tin, and iron. (c) As to the best method of determining by volumetric analysis, or other means, their relative mordanting power.

The Silver or Bronze Medal of the Society for the best critical essay (not exceeding 10,000 words) on the treatment of effluents from dyehouses and textile factories.

Prize of £20 for a determination of the average degree of diminution in strength of three-standard cotton yarns, *e.g.*, 2/40's American, 1/50's Egyptian, 2/120's

Sea Island, brought about by different bleaching processes.

Prize of £20 for a full investigation of the average degree of tendering brought about in cotton yarn by—(a) Cross dyeing with acid colours; and (b) Dyeing Aniline Black; with the object of fixing standards for the trade.

Prize of £30 for a practical method of causing kemps, when present in yarn or piece goods, to take dye-stuffs equally with the accompanying wool.

Prize of £20 for a practical method of dyeing full shades of basic colours on cotton fast to rubbing.

The Silver or Bronze Medal of the Society and £20 for a full investigation of the influence of the various substances present in natural Indigo in respect to their influence upon the dyeing of wool by the fermentation vat, and the depth, bloom, and fastness of the shade obtained.

The rules governing the award of the prizes and general conditions to be fulfilled by competitors may be obtained on application to the Hon. Sec., Mr. ERNEST T. HOLDSWORTH, Pearl Assurance Buildings, Market Street, Bradford.

The Dyers Company's Research Medal.—The Worshipful Company of Dyers offer a Gold Medal to be awarded by the Council of the Society of Dyers and Colourists. The Medal will be known as "The Dyers Company's Research Medal," and will be given for "the best scientific or technical investigation connected with the tinctorial arts" submitted to the Society for publication before December 31st, 1909.

Blackening and the Properties of Leather.—J. C. Thomlinson.—With poor varieties of leather I have found ordinary blackening to give the appearance of black-lead. A suitable application of grease (any animal fat), with only an occasional use of blackening, keeps leather which otherwise appears of a poor quality in a more perfect condition; in fact, gives it all the appearance of what is commonly regarded as first-class leather. I am not aware how far almost all varieties of leather may not be in a more or less finished condition when used for manufacture. Hence such an application as the above conduces to preserving and giving a proper finish.

"The Annals of Psychological Science," founded in January, 1905, has changed hands. Mr. Dudley Wright, the present assistant editor, has succeeded Mrs. Laura I. Finch as editor, the last named joining the Editorial Board, which already includes such well-known names in the world of psychical research as Camille Flammarion, Prof. Lombroso, Prof. Charles Richet, and Col. Albert de Rochas. Premises have also been secured in the west-end of London for the proposed Psychological Research Club which will now shortly be opened. Mr. Wynton Hope has been appointed Secretary, and all communications respecting the Club should for the present be addressed to him, care of "The Annals of Psychological Science," 110, St. Martin's Lane, London, W.C.

NOTICE.

The STUDENTS' NUMBER of the CHEMICAL NEWS will be published on Friday, September 17th. Gentlemen holding official positions in the Universities, Medical Schools, &c., of the United Kingdom, where Chemistry and Physical Science form a part of the education, who have not yet forwarded the necessary information to our Office for publication in that Number, will confer a favour by sending it with the least possible delay.

Advertisements for this Number should reach the Office not later than TUESDAY, Sept. 14.

THE CHEMICAL NEWS.

VOL C., No. 2597.

ADDRESS TO THE CHEMICAL SECTION OF THE BRITISH ASSOCIATION.

WINNIPEG, 1909.

By Prof. H. E. ARMSTRONG, Ph.D., LL.D., F.R.S.,
President of the Section.

It is recorded that, on a certain occasion, after saying, "I shall not often give arguments but frequently opinions—I trust, with courtesy and propriety, &c.," a professor of world-wide reputation remarked, "A man's opinions, look you, are generally of much more value than his arguments. These last are made by his brain, and perhaps he does not believe the proposition they tend to prove—as is often the case with paid lawyers; but opinions are formed by our whole nature—brain, heart, instinct, brute life, everything all our experience has shaped for us by contact with the whole circle of our being."

Of his many charming utterances at the breakfast table, I would select this as one of the most noteworthy and just withal. Chemists especially need to take both opinions and feelings into account, as well as arguments; to appreciate more fully, perhaps, than is now customary, the need of cultivating and giving expression to that state of mind which is the main qualification of the expert—the state of mind which, let me insist, in the case of the chemist, is only to be acquired by constantly associating with and constantly handling substances in being and in the making, by constantly striving to become acquainted with their innermost nature and idiosyncrasies. It is safe to say that much of the subject matter of our science is not yet quantifiable and probably never will be; it is even easy to overrate the value of quantitative measurements, as the processes studied, more often than not, are involved operations that can be only with difficulty, if at all, resolved into their factors.

After an interval only a year short of a quarter of a century, it is my privilege again to occupy the chair of this Section and that, too, under conditions of special significance. The British Association has never before sought to carry the banner of science so far west into British Dominions—never before was it so clear that the progress of humanity is linked with the progress of science by an indissoluble bond; science defined in a word being *knowledge*, not mere work nor mere lip knowledge, but systematised established knowledge, not assumed knowledge—although hypothesis often serves to guide inquiry and truth is arrived at only gradually and slowly by a series of rough approximations. Moreover, science is true knowledge of every kind—there is too often a tendency to give a narrow interpretation of the word. One reason probably why the term does not produce any proper effect upon the average British ear is that it is not an English word but a mere adaptation from the Latin—a language which apparently cannot be engrafted upon our Saxon tissues, although, perhaps, it may be that we have so little feeling for it because we have been allowed to learn so little else in our higher schools; monotony of diet ever favours diminutive growth. Germans, I always feel, enjoy a great advantage over us in possessing the popular word *Wissenschaft*—in calling science the *business of knowing*, the *business of gaining wisdom*, of being wise.

Coming as we do to Canada to advocate such a cause, to direct attention to the principles on which alone such a business can be learnt and conducted with profit—surely we may count on meeting with the support of the public at large: it is this we desire and claim—not merely the sup-

port of a few specialists; moreover, we do not ask for it in any way as a favour but practically demand it as a right—in no way, however, on personal grounds or with any display of arrogance, but because we are persuaded that our message is of such infinite importance to the well-being of the community that it is our clear duty to make it of avail. Here it is that opinion, not argument, must count; the language of science is and must remain, in many ways, a strange one to the public; we must therefore ask that they entrust us with their confidence and allow themselves to be guided by the experience we have gained; we must be as the prophets of old: regardless of consequences, we must insist on the overthrow of the idols which a narrow priesthood still attempts to force upon society. We need always remember that, as my good friend the Professor expresses it—"Man is an idolator or symbol-worshipper by nature, which, of course, is no fault of his, but sooner or later all his local and temporary symbols must be ground to powder, like the golden calf—word-images as well as metal and wooden ones." It is, as he says, "Rough work, Iconoclasm—but the only way to get at Truth."

Naturally I am constrained on the present occasion to take stock of the position of our science, to draw a comparison between the condition of affairs chemical when we met in Aberdeen in 1885 and their present state. No like period of human history has been more fruitful of advance; at the same time, no period illustrates more clearly the difficulties that lie in the path of progress—because of the innate conservatism proper to human nature.

It was my privilege in 1885 to discuss a variety of problems which then seemed to be of special importance in relation to the subject of Chemical Change, our main province of study. I find the same problems dominant now—still unsolved but yet nearer solution. The history of progress, of discovery, during the intervening period is wonderfully rich in incident—how rich perhaps few realise, as it is obscured by a mass of blinding detail. If I attempt to bring some of the scattered threads together and in so doing dare to paint a picture which here and there may be startling in its outlines and implications; if I venture to follow the example set by one who has appeared as an autocrat as well as a professor and sometimes give my naked opinions: it will, I trust, be understood that I do so conscious that the sketch I am presenting must be full of the faults to which all such attempts are subject.

In my previous Address two very different topics were considered—the Educational Outlook and the Theory of Chemical Change. In dealing with the former, I drew special attention to the need of creating an atmosphere of research in our colleges—then to the faulty curriculum of our schools and the need of introducing reforms into practically every branch of education, especially medical education. In the interval, considerable progress has been made by way of forming plans for the future, even a foundation stone or two has been put in place, although scarcely "well and truly laid"—but the actual buildings are hardly marked out. In point of fact, the needs to which I called attention in 1885 are our present and now most urgent needs. But of this more subsequently.

In discussing chemical action, I commented on our failure to arrive at any understanding as to the conditions which determine the occurrence of chemical change—a failure all the more remarkable in view of the clearness of Faraday's early teaching. Basing my remarks on the thesis which he propounded in 1834 that the forces termed electricity and chemical affinity are one and the same, I discussed current views on electrolysis and arrived at a conclusion entirely adverse to the explanation put forward by Clausius that the conductivity of electrolytes was conditioned by the presence of a small proportion of separate ions; this was at a time when the views of Arrhenius were not yet spread abroad, although they had been communicated to the Swedish Academy; I knew of them only from Ostwald. In justice to the attitude of complete antagonism

which I have always maintained towards the speculations of the Arrhenius-Ostwald school, I may point out here that in drawing attention to the views expressed by Arrhenius and Ostwald as to the correlation of chemical with electrolytic activity (and I was the first English writer who called attention to them), I took occasion to say: "There cannot be a doubt that these investigations are of the very highest importance." In the interval, Ostwald has charged his test-tubes with ink instead of with chemical agents, and by means of a too facile pen has enticed chemists the world over into becoming adherents of the cult of ionic dissociation—a cult the advance of which may well be ranked with that of Christian science, so implicit has been the faith of its adherents in the doctrines laid down for them, so extreme and narrow the views of its advocates. At last, however, the criticism which has been far too long delayed is being brought to bear and the absurdity of not a few of the propositions which the faith entails is being made evident; it is to be hoped that we shall soon enter on a period in which common sense will once more prevail; that ere long an agreement will be arrived at, both as to the conditions which determine it and as to the nature of chemical change in general. The lesson we shall have learnt is one of no slight import if it but teach us the ever-present need of questioning our grounds of belief, if it serve to bring home to us the danger of uncontrolled literary propagandism in science, if it but cause us always to be on our guard against the intrusion of authority and of dogmatism into our speculations.

Before attempting to deal with any of the problems which concerned us at Aberdeen I will first briefly pass the more salient features of advance in review. Few probably are aware how extraordinary is the command we now have of our subject. In 1885, in defending the tendency of chemists to devote themselves to the chemistry of carbon, I could speak of the great outcome of their labours as being the establishment of the doctrine of structure. Everything that has happened in the interval is in support of this contention. It is interesting that in a recent lecture on the Physical Aspect of the Atomic Theory (the Wilde Lecture, 1908, by Prof. Larmor, Sec. R.S., *Manchester Literary and Philosophical Society Memoirs*), the most prominent living exponent of physical theories has given a not unwelcome recognition of our right-mindedness in saying: "As time goes on it becomes increasingly difficult to resist the direct evidence, for the simple view that, in many cases, chemical combination is not so much a fusion or intermingling of the combining atomic structures as rather an arrangement of them alongside one another under steady cohesive affinity, the properties of each being somewhat modified, though not essentially, by the attachment of the others; and that the space formulæ of chemistry have more than analogical significance." And again in the following passage, in which a far-reaching confession is made: "The aim of structural chemistry must go much deeper (than dynamical methods of treatment); and we have found it difficult, on the physical evidence, to gainsay the conclusion that the molecular architecture represented by stereo-chemical formulæ has a significance which passes beyond merely analogical representation and that our dynamical views must so far as possible be adapted to it." The remark made by Helmholtz in one of his letters, "that organic chemistry progresses steadily but in a manner which, from the physical standpoint, appears not to be quite rational," must be regarded as little more than a confession that he was out of his depth. When properly understood, nothing could be more rational and logical than the way in which our theory of structure has been gradually built up on an impregnable basis of fact, with the aid of the very simple conceptions of valency postulated by Frankland and Kekulé. Our security lies in the fact that the postulates of our theory have been tested in an almost infinite variety of cases and never found wanting; this is not to say they are applicable in all cases, but merely that whenever we

are in a position to apply them we can do so without hesitation. Larmor refers to the habit of physicists of taking comfort in Helmholtz's remark; it will be well if instead they make themselves acquainted with our methods and with the results we have won, with a minimum of speculative effort, by the cultivation of an instinct or sense of feeling which experience shows to be an effective guide to action. Now that physical inquiry is largely chemical, now that physicists are regular excursionists into our territory, it is essential that our methods and our criteria should be understood by them. I make this remark advisedly, as it appears to me that of late years, while affecting almost to dictate a policy to us, physicists have taken less and less pains to make themselves acquainted with the subject-matter of chemistry and especially with our methods of arriving at the root-conceptions of structure and of properties as conditioned by structure. It is a serious matter that chemistry should be so neglected by physicists and that the votaries of the two sciences should be brought so little into communion.

The central luminary of our system, let me insist, is the element carbon. The constancy of this element, the firmness of its affections and affinities, distinguishes it from all others. It is only when its attributes are understood that it is possible to frame any proper picture of the possibilities which lie before us of the place of our science in the Cosmos. But, as Longfellow sings of the sea in his poem "The Secret of the Sea," "Only those who brave its dangers comprehend its mystery"—only those who are truly conversant with the root conceptions of organic chemistry are in a position to attempt the interpretation of the problems of our science as a whole or even to understand the framework upon which it is built up. And yet we continue to withhold the knowledge of the properties of carbon from students until a late period of their development; indeed, when I insisted recently that organic and inorganic chemistry should be taught as one subject to medical students ("The Reform of the Medical Curriculum," *Science Progress*, January and April, 1907), I was told that it could not be; that the attempt had been made with disastrous consequences. I trust that ere long the futility of such an attitude will be generally realised.

It is remarkable how much our conceptions are now guided by geometrical considerations. The development by van't Hoff of the Pasteur hypothesis of geometrical asymmetry has been attended with far-reaching consequences during the period under review, the completeness with which the fundamental properties of the carbon atom are symbolised by a regular tetrahedron being altogether astounding.

Our present conception is that the carbon atom has tetrahedral properties in the sense that it has four affinities which operate practically in the direction of the four radii proceeding from the centre towards the four solid angles of a regular tetrahedron.

More than analogical significance—to use Larmor's expression—must be accorded to this symbol on account of its remarkable accordance with the facts generally, whether derived from the study of asymmetric optically active substances or from observation of the activity of ring structures of various degrees of complexity. Nothing is more surprising than the completeness with which the vast array of facts included in organic chemistry may be ordered by reference to the tetrahedral model. In the future, when our civilisation is gone the way of all civilisations and strangers dig on the sites of our ruined cities for signs of our life, they will find the tetrahedron and the benzene hexagon among the mystic symbols which they have difficulty in interpreting; if, like the ancient Egyptians, we made our tombs records of our wisdom, such symbols would long since have acquired sacred significance and the public would probably have learnt to regard them with awe and to respect them as totems. Chemists might at least wear them on aprons in imitation of the Freemasons—perhaps not two other symbols have so great a significance—they reach into life itself.

It would seem that carbon has properties which are altogether special, the influence which it exercises upon other elements in depriving them of their activity is so remarkable. In their recent discussion of the relation of crystalline form to structure, in which valency is represented as a function of the volume sphere of influence exercised by an element, Barlow and Pope arrive at the remarkable conclusion that carbon is probably the only element the atom of which has a volume sphere of influence four times that of the hydrogen atom; although it combines with four atoms of hydrogen, silicon apparently has only half the volume sphere of influence of carbon. This may, in a measure, account for the very great dissimilarity in behaviour of the two elements, which is most pronounced in their oxides, the single atom of carbon all but dominating two atoms of oxygen in carbon dioxide (which is consequently gaseous), whilst the atom of silicon in silicon dioxide in no way eclipses the two atoms with which it is associated, but leaves both charged with residual affinity which enables them to form complex collocations of remarkable fixity in the fire. At bottom the differences between organic and inorganic nature are to be regarded as very largely the expression of this difference. Ropes of sand are proverbially treacherous; yet without sand, if silica had been a gaseous substance, our world might have worn a strangely different aspect (see Note 1).

The mineral world apparently owes its rigidity to the fact that the metals and certain other elements are so imperfectly capable of dominating oxygen that oxides generally polymerise with great readiness, giving rise to substances which do not even fuse easily. The organic, on the other hand, appears to be plastic by reason of the close approach to neutrality which is conditioned by association with carbon.

Nothing is more striking than the remarkable diversity of properties manifest both in the materials which at present we are content to call elements and in the compounds formed by their interaction; the range of variation met with in the case of the compounds of carbon with hydrogen and oxygen alone is almost infinite. We are almost compelled to attribute this diversity more to differences in the complexity and structure of the molecules than to differences in their material composition. The chemist, of necessity, must be a dreamer, knowing as he does that things are not as they seem to be. But this is not sufficiently remembered; indeed, students are systematically trained up in an atmosphere of pretence. The beginner is allowed to regard *elementary oxygen*, for example, as a colourless gas, which is generally harmless until things are presented to it in a more or less heated condition, whereat it takes umbrage and burns them up. He would regard elementary carbon as a soft black substance, which if smeared on the face of the white man makes him look like a nigger, were it not that he also learns that at times it is the hardest and whitest substance known; of organic chemistry, which alone can give him honest ideas of carbon, he is not allowed to hear as I have said. The sting of awakening conscience is salved by the introduction of a long Greek word when he is told that the two substances, soot and diamond, are *allotropic* forms of the element carbon; nevertheless, he regards them both as elementary carbon. Gradually, perhaps, he awakens to a sense of the wrong that he has suffered at the hands of his teachers, as he realises that from no one substance can he gather what the properties of an element are, that after all the elementary substance is but an ideal—in other words, a mere concept. If appreciative, he then learns to think of the blandness of water, the sweetness of sugar, the sourness of vinegar, the causticity of soda, indeed every distinctive property of every known oxygen compound as more or less a property of, more or less conditioned by, the element oxygen, he is brought back, in fact, to the position from which Lavoisier started, as he realises that the oxygen gas which he inhales is not elementary oxygen; he can then perhaps appreciate the wonderful

acumen which this greatest of chemical philosophers displayed when he wrote:—"Nous avons donné à la base de la portion respirable de l'air le nom d'oxygène en le dérivant de deux mots grecs *ὀξύς*, acide, *γεννῶμαι*, j'engendre, parce qu'en effet une des propriétés les plus générales de cette base est de former des acides en se combinant avec la plupart des substances. Nous appellerons donc gaz oxygène la réunion de cette base avec le calorique." We have allowed a century to pass without recognising the wonderfully accurate powers of prevision displayed by Lavoisier; what is worse, we have been so far led astray that instead of regarding oxygen as the characteristic and attractive element in acids, hydrogen has been allowed to usurp the position: the extent to which the cult of the hydrogen ion now dominates the text-books is well known; in days to come, when the history of our times is written, it will be referred to as a remarkable example of chemical shortsightedness.

Names are needed for the elements which would serve to distinguish the ideal elementary substances from the forms in which they are known to us. No more appropriate name than oxygen could possibly be selected for the fundamental material; if the *gen* terminal could be applied to elementary materials generally, it would be an advantage; it would not be easy, however, if this were done, to devise an appropriate separate name applicable to the active constituent of air (see Note 2).

In 1885 I closed my address with a reference to the structure of the elements which implied that their behaviour was that of compound substances; the feeling that this is the case has long been general among chemists. Our present attitude towards this problem is a curious one and not altogether satisfactory—it is impossible to deny that we have somewhat lost sense of proportion, even if our methods have not savoured of the unscientific. The discovery of radium appears to have upset our balance—we have been carried away by the altogether mysterious and unprecedented behaviour of this weird and wondrous substance. But may we not ask: Is radium an element? Has it not been too generally, too hastily assumed that it is? Little as we know of it, does not its behaviour straightway outclass it as an element? Surely it does! Is not the established fact that an emanation proceeds from it, which in turn decomposes and gives rise to helium, a proof of its compound nature? Again, is the evidence of such a character as to justify us in asserting that uranium is the parent of radium? If it be such, must not uranium also disappear from the list of elements; must it not indeed be removed on the ground that it gives rise to uranium without any reference to its supposed relationship to radium?

The answers given to such questions must depend on our definition of an element. At present we seem to be without one.

The conception that the break-down of radium is spontaneous and apart from all external impulse or control is also one which should be received with caution. There is reason to suppose that in all ordinary cases in which compounds undergo decomposition spontaneously, the decomposition is conditioned by an impurity; the effect, moreover, is usually cumulative. This is true of highly explosive substances, such as chloride of nitrogen and gun-cotton, for example. It might be supposed that something similar would happen in the case of radium—but apparently such is not the case; it is assumed that occasionally a molecule explodes spontaneously, not only without being incited thereto but also without in any way affecting its neighbours.

The alternative explanation that radium in some way acts as a receiver, transforming energy from some external source to which ordinary substances fail to respond and being thereby stimulated to decompose, is at present out of favour, although perhaps more in accordance with its peculiar behaviour (see Note 3).

The liberation of helium as a product of radio-active change is in itself a significant fact, in view of the possibility that helium may be an element of intense activity. Nothing in connection with the problem is more surprising,

however, than the apparent production, in course of time, of a whole series of degradation products which differ greatly in stability—such behaviour is entirely without precedent and not at all becoming in elements.

No such remarkable and inspiring problem has ever before been offered for solution. We can only wonder at the results and admire the genius which some have displayed in interpreting them, Rutherford in particular. Yet outsiders may well hold judgment in suspense for the present; whilst it is permitted to workers to make use of hypothesis in every possible way in extending inquiry, the public are in no wise called upon to accept such hypothesis as fact.

But apart from the suggestion that elements may give rise to others spontaneously, we have been entertained of late with stories of elements being converted into others under the influence of the energy let loose by the breakdown of radium. There is reason, however, to suppose that the powers of radium may have been greatly over-painted; energy of almost any degree of intensity in the form of high tension electricity is now at our disposal, and the effect which radium produces on living tissues, glass, &c., is of the same character as that effected by the Röntgen ray discharge, the only difference being that the effect is produced somewhat more rapidly; it is not to be imagined, therefore, that the discovery of radium has put any very novel intensity of power into our hands.

It is right that the public should understand that the statements published have been based on preliminary observations which lack verification, such as would never have been divulged in days gone by when a sterner sense of duty pervaded our ranks. Until the elementary nature of radium has been placed beyond question, we must hold judgment in suspense even as to the possibility of "elements" undergoing decomposition "spontaneously"; at present, the possibility of elements being decomposed or transmuted by means of radium need not be entertained until evidence is forthcoming of a more convincing character than that with which we have been favoured.

We have been living in a time of sensational discovery—in a period when advertisement is favoured and the desire for notoriety rampant. Unhappily, that caution which appeared to be regarded as a priceless prerogative of the scientific worker in the earlier part of the last century, of which Faraday was so pre-eminent an exponent, is no longer our recognised watchword. I fear I am one of those who are old-fashioned enough to lament the way in which our claim to be safe and honest guides of public opinion is being endangered—who lament the manner in which the reputation of scientific workers is likely to be besmirched if we do not see the evil of our ways and mend them. It is impossible to avoid noticing how the cancer grows—how the example is spreading among the younger men, and loose habits of work and thought are being engendered. I know that not a few who have laboured steadfastly and seriously in an old-fashioned exact and painstaking way, have been deeply hurt by the manner in which their efforts fail to meet with encouragement whilst those who have thrown caution to the winds are favoured; the feeling is beginning to arise that only sensational discovery is appreciated by the public. We need to return to the healthy times when fearless and frank criticism of all work was deemed desirable. We cannot substantiate the claims that are made on behalf of science unless our own attitude be above reproach—unless we are both logical and philosophical—unless we remain the sternest advocates of truth in its most rigid form.

I pass to the consideration of the classification of the elements. The recognition of certain properties, the association of certain ideals with the several elements, is a necessary step in classifying the elements in accordance with Mendeleeff's great generalisation—or rather it may be said to be both involved in, and an outcome of, Mendeleeff's conception.

Until recently our difficulty was to understand the

relationship of the metallic and the non-metallic elements; now we are confronted with another problem—that of the existence of inert "paraffinoid" elements. It is commonly assumed that these are monatomic, but the evidence on which this assumption is based is absolutely unconvincing, and would be generally admitted to be so were we in the habit of looking before we leapt to conclusions. Assuming that the elements are compounds, the formation of inert compounds does not appear to be out of place, in view of the existence of practically inert hydrocarbons. But, on the other hand, in view of the properties of nitrogen, which is one of the most active of substances in the monatomic state, although an inert gas in the diatomic condition, it may well be that the inertness of helium and the other members of the argon group is also simulated. Sir James Dewar's observations have shown that helium and charcoal have no inconsiderable affinity at the boiling-point of the former, which is within 5° of the absolute zero, the molecular heat of absorption (apart from that due to liquefaction) of helium at that temperature being apparently as high as about 60 calories. The proof he has also given that helium alone does not convey an electric discharge is also of significance since the passage of a discharge through it under ordinary conditions is an indication that it can be included with other substances in a conducting system. Such evidence as there is therefore points to the elements under discussion being different from the others only in the degree of stability of their molecules.

Of late years the difficulty of classifying the elements has been increased rather than diminished, not merely because of the discovery of the inert gases but also on account of the apparent impossibility of ordering the position of an element such as tellurium in accordance with its atomic weight. There appears to be little room left for doubt that the value cannot be far removed from that of iodine; it should be considerably lower. It may be pointed out that the accepted value of selenium is closer to that of bromine than would be expected if a relationship were maintained corresponding to that between chlorine and sulphur. It would seem that Mendeleeff's original conception of the elements as a simple series in which the properties are periodic functions of the atomic weights must be abandoned in favour of some more comprehensive scheme. From the chemist's point of view, it is impossible to abandon the guiding principle underlying the arrangement in family groups, which dates back to Dumas; perhaps insufficient attention has been paid in the past to the maintenance of this principle.

Taking into account this principle, it is impossible to arrange a long series of elements such as the rare earths continuously in order of atomic weight, as they would be brought into every family in the table by such a procedure; the difficulty has been got over by Brauner, who has proposed to arrange a large number of the rare earths in a single vertical series under barium. Biltz has made a similar proposal.

The principle has been advocated by me previously in an article written for the "Encyclopædia Britannica" (*cf. Roy. Soc. Proc.*, 1902, lxx., pp. 86–94).

In the arrangement I have proposed, it is not only assumed that there may be as many as sixteen vertical series of elements of which the elements from hydrogen to oxygen are initial terms, some series being at present unrepresented, it is also suggested that groups of elements occur in perhaps four of these series, numbers 4, 8, 12, and 16, the largest being that of the so-called rare earths in series 8.

The principle which is assumed to be in operation is that which is so clearly manifest in the case of hydrocarbons: successive vertical series of elements correspond to successive isologous series of homologous hydrocarbons. In the case of the hydrocarbons, the passage from one isologous series to another often takes place from a term several places removed from the origin of the series—for example, from benzene, C_6H_6 , which may be regarded as primarily a derivative of hexane to naphthalene, $C_{10}H_8$,

which is not an immediate derivative of benzene but of butylbenzene. It is conceivable that at the genesis of the elements a process was at work corresponding to that by which a hydrocarbon, such as naphthalene, is derived from benzene, and by which the former then serves in turn as the point of departure for more complex hydrocarbons of other series. There is no reason, from this point of view, why progression should not take place along a particular line, and that terms should exist in a series through which this line passes but below it—for example, that antimony and iodine may bear a direct linear relationship, but that tellurium, instead of being the element in the progression series in the oxygen group, is a homologue of greater weight. The same view may be taken of selenium. In this way, it would be possible to maintain selenium and tellurium in the oxygen-sulphur series, from which they cannot well be separated, whilst retaining Mendeleeff's conception of a genetic relationship along the series. The only departure involved is in assuming that instead of forming a single linear series ascending regularly in spiral progression—a series which can, as it were, be strung on a single spirally wound cord—the elements closely simulate a series of homologous isologous hydrocarbons. From this point of view, it is easy also to understand that some vertical series are unrepresented.

In discussing the chief attributes of the elements none is so difficult to deal with as that of valency, using the term in the broadest possible sense, not merely as indicative of the number of units of affinity but as including the, at present, all but incomprehensible problems of residual affinity and elementary character. I discussed the subject somewhat fully in my former Address, dwelling especially on the properties of negative elements and their power of acting as linking agents; this view has met with ample confirmation in the interval, and will, I believe, be found to be of wide application in the future. I have already referred to the manner in which it is exemplified by silica.

The greatest advance in the discussion of the problems of valency in recent years is that made by Barlow and Pope, as their method of treatment is one which applies to solid substances—the correlation of structure with crystalline form which it effects promises to be of far-reaching importance.

Apart from hydrogen, carbon is the one element of certain character, always acting as a tetrad—its affinities may be only incompletely satisfied, but they are always exercised, it may be supposed, even in ethenoid and similar compounds; carbon monoxide apparently is the only exception to this rule, its relative inactivity being one of the most puzzling enigmas of our science, especially as the oxide becomes one of the most active of known substances when only two atoms of hydrogen are added to it. Most other elements (non-metallic) seem to vary in valency, the valency beyond a certain minimum being dependent on the nature of the association. Of late years, attention has been drawn in particular to the quadrivalency of oxygen in many of its compounds.

The quadrivalency of sulphur in substances such as trimethylsulphonium iodide, Me_3SI , having been proved to demonstration by the production of optically active compounds of this type (Pope and Peachey), it can no longer be supposed that in such cases we are dealing with compounds in which the negative constituents of the parent molecules are conjoined, e.g., $\text{MeI}:\text{SMe}_2$. And yet we must contemplate the existence of such compounds as possible—in the case of nitrogen, for example, as ammonia must be supposed to form the compound $\text{NH}_3:\text{OH}_2$ in preference to the hydroxide $\text{NH}_4.\text{OH}$, the latter being only a very minor constituent, the former the major component of the aqueous solution of the gas; hydrogen chloride, on the other hand, appears only to afford one product with ammonia, viz., $\text{NH}_4.\text{Cl}$. The existence of such differences affords clear proof in the case of the non-metallic elements

other than carbon that valency is not merely a variable but also a reciprocal or dependent function.

There is no reason to suppose that hydrogen ever acts otherwise than as a simple monad; and the behaviour of the alkalis and alkaline earths in salts would seem to justify the conclusion that they have no tendency to vary in valency, were it not for the existence of well-defined non-volatile hydrides of these metals which are clearly substances of some degree of molecular complexity. Such compounds are illustrations of the difficulties which surround the subject. It has long been clear that the exhibition of the higher valency by an element is a process of a different order from that manifest when it exerts only its lower proper valency measured in terms of positive radicles such as H or $\text{C}_n\text{H}_{2n+1}$ radicles. What that difference is we are not able at present to decide—carbon (together with silicon) differs from almost all other elements especially in combining with hydrogen and analogous radicles to the extent of its maximum valency.

The proposition I made in 1888 (*Phil. Mag.*, Series 5, xxv., 21) that the valency lines should, in some cases, be represented as passing through the atom, so that each is capable of acting in two directions, is the only consistent mode of expressing varying valency which has been devised, the only one, moreover, by which attention is drawn to the great difference.

In many cases probably there has been a tendency to exaggerate the valency value—in the case of chlorine, for example, in assuming that it functions as a heptad in the perchlorates. In this and many other instances, it suffices to assume that the chlorine and oxygen atoms are united in a closed ring, the chlorine functioning as a triad. Some such explanation will doubtless be given of the structure of the metallic ammonias and similar compounds. The co-ordination values introduced by Werner serve only to establish certain empirical relationships, and are useful for the purposes of classification. The perhaps more rational plan of dealing with such compounds suggested by Abegg has a similar value.

It is to the advantage of the hypothesis formulated by Barlow and Pope that the elements are represented as of constant valency in so far as their relative volume spheres of influence are concerned—the compound in which the higher valency is manifest being derived from that of lower valency by the opening out of the close packed arrangement and the insertion of certain new elements; but the fact that in such cases the volume is altered not in one direction alone in the crystalline structure but proportionately in all directions, would seem to show that the volume sphere of atomic influence does actually change; the change is one, however, which affects all the atoms in the complex proportionately.

At present, unfortunately, our methods of treating the problems of valency are such that we cannot in any way give expression to the energy side of the phenomena.

Of late there has been talk of electrons in this connection, but what is said is little more than superficial paraphrase, in the advanced scientific slang of the day, of the ideas which have long been current. When, following Odling, we represent valency by dashes written after the elementary symbol, we give clear expression by means of a simple convention to certain ideas that are well understood by all among us who are versed in the facts; to speak of electrons and use dots instead of dashes may serve to mislead the unwary, who hang on the lips of authority, into a belief that we have arrived at an explanation of the phenomena, but those who know that we have reached only the let-it-be-granted stage and who feel that the electron is possibly but a figment of the imagination (see Note 4), will remain satisfied with a symbolic system which has served us so long and so well as a means of giving simple expression to facts which we do not pretend to explain. Not a few of us who listened to the discussion of the nature of the atom at Leicester could not but feel that the physicists knew nothing of its structure and were wildly waving hands in the air in the endeavour to grasp at an interpretation which would

permit of mathematical interpretation being given to the facts. Until the credentials of the electron are placed on a higher plane of practical politics, until they are placed on a practical plane, we may well rest content with our present condition and admit frankly that our knowledge is insufficient to enable us even to venture on an explanation of valency.

In 1885 and again in 1888, I ventured to call in question the interpretation of valency which Helmholtz had given in the Faraday lecture in 1881. On the present occasion I would insist still more emphatically on the insufficiency of the atomic charge hypothesis; especially that it affords no satisfactory explanation of variable valency and of those fine shades of difference which are manifest, especially in the case of nitrogen, when the radicle attached to the dominant element is varied. In 1885 I discussed this question with reference to the nature of electrolytes and questioned the conclusion Helmholtz arrived at that electrolytes belong to the class of typical compounds the constituents of which are united by atomic affinities, not to the class of molecular aggregates. The opinion I then ventured to give was as follows:—

"The current belief among physicists would appear to be that primarily the dissolved electrolyte—the acid or the salt—is decomposed almost exclusively. We are commonly told that sulphuric acid is added to water to *make it conduct*, but the chemist desires to know why the solution becomes conducting. It may be that in all cases the 'typical compound' is the actual electrolyte—i.e., the body decomposed by the electric current—but the action only takes place when the typical compounds are conjoined and form the molecular aggregate, for it is an undoubted fact that HCl and H₂SO₄ dissolve in water, forming 'hydrates.' This production of an 'electrolytical system' from dielectrics is, I venture to think, the important question for chemists to consider. I do not believe that we shall be able to state the exact conditions under which chemical change will take place until a satisfactory solution has been found."

The position is not very different now. Although the propagation of the ionic dissociation cult has assumed the form of a fine art, we are still as far as ever from agreement as to the nature of chemical change; the speculation has not helped us in the least to clarify our ideas; at most we learn that interactions are between ions, and even these, as a rule, are supposed to remain apart until they enter into the solid state. Throughout all these years I have never varied my opinion that the dissociation hypothesis is incompatible with the facts. On more than one occasion I have stated definite reasons which induce me to deny its usefulness (see Note 5) and these arguments have never been met; in fact, there has been little but a conspiracy of silence on the part of the upholders of the creed.

A large amount of work bearing on the subject has been done, chiefly by H. Brereton Baker. Strangely enough, no proper notice of his results has been taken outside England, and even there the importance of the observations has not been sufficiently appreciated. Perhaps the most remarkable feature in the situation is that Baker himself scarcely seems to be alive to the meaning of the evidence which he has supplied; the attitude which he has displayed in his recent Wilde lecture can only be described as halting. Baker has shown, in case after case, that the occurrence of change is dependent on the presence of moisture, his greatest feat perhaps being the observation that it is possible not only to prepare nitrous anhydride in the solid and liquid states but to volatilise it unchanged if only water be excluded.

I venture to think there is only one point of view from which the problem of chemical change can be approached, that, namely, which we owe to Faraday—to which hitherto justice has in no way been done—on which I dwell persistently in my previous address: that the forces termed chemical affinity and electricity are one and the same. In every case of chemical change there is a coincident electrical change, an electric flux; on the other hand, every

case of electrical change is accompanied by chemical change, some alteration in molecular configuration is effected; the force of chemical affinity is in some way disturbed by a momentary displacement of the molecules when a current passes through a conductor. Such being the case, the conditions determinative of chemical change can only be those which permit of an electric flux. Two substances in apposition do not give rise to a current; at least three are required to determine a slope of potential. Chemical change can only take place if one of the three be an electrolyte. In all cases apparently the chemical change supervenes upon the electrical, the electrolyte being resolved into its ions, one of which at least combines coincidentally with the adjacent electrode. Apparently these considerations are applicable to changes generally. And it should be added that, according to this view, the catalyst actually determines the occurrence of change.

The only other criterion which it is necessary to apply in order to decide whether change be possible in any given case is to consider if the change contemplated be one involving development of energy. It is important to remember also that a change which could not otherwise take place becomes possible when a suitable depolariser is introduced into the circuit.

The evidence that similar considerations apply to the gaseous and the liquid states cannot well be gainsaid. Before framing a theory of chemical change it is therefore necessary to formulate a definition of an electrolyte. It is doubtful if any single substance be an electrolyte; the conductivity of fused salts may well be and probably is conditioned by some admixture. Aqueous solutions of alkalis, acids, and salts without exception are electrolytes. *Everything points to the fact that in such solutions the solvent and solute act reciprocally; the contention that the solute alone is active cannot be justified.* As water is altogether peculiar in its activity as a solvent and is a solvent which gives rise to conducting solutions, an explanation of its efficiency must be sought in its own special and peculiar properties.

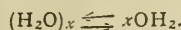
Since 1880 this conclusion has been impressed upon me with indisputable force, and I have frequently ascribed the effect produced by the one constituent upon the other in a solution to the residual affinity of the negative elements in the two compounds which act reciprocally. It was only recently, however, that I saw my way to postulate a complete theory which would serve to account for the properties of solutions and generally that I realised how the reciprocal effect might be produced.

I would substitute for the misleading conception that liquids are comparable in their behaviour with gases the idea that the liquid state is one in which the residual affinity of the negative elements in particular always comes into play and causes the formation of molecular aggregates of various degrees of complexity; moreover, that the alteration in the properties of any given solvent by the dissolution in it of another substance is largely, and in some cases mainly, due to a disturbance of the equilibrium natural to the solvent by an alteration in the proportion in which the several aggregates are present. The alteration in some particular property produced in a given mass of the solvent may, from this point of view, be taken as the measure of the activity of a substance, just as the alteration in the pressure of a particular volume is taken as the measure of the alteration produced in a gas. In the case of non-electrolytes, if only a small amount of the solvent be withdrawn by combination with the solute, the alterations may be regarded as almost entirely due to the "mechanical" interference of the substance introduced, opportunity being given for the simpler, more attractive molecules of the solvent to exist in greater proportion because of the diminution of the chance of reuniting which is conditioned by the presence of practically inert molecules of another kind; if a more or less considerable amount of the solvent become associated with the solute the conditions become more complex, but similar considerations apply. From such a point of view a liquid is rendered

more active by the addition of any soluble substance. Its vapour pressure is therefore diminished; the internal "osmotic" stresses are raised; its freezing-point is lowered.

Although it is generally admitted that water is not a uniform substance but a mixture of units of different degrees of molecular complexity, the degree of complexity and the variety of forms is probably underestimated and little or no attention has been paid to the extent to which alterations produced by dissolving substances in it may be the outcome and expression of changes in the water itself. The attempt to extend the "laws" which are applicable to the gaseous state to liquids has led us away from the truth by narrowing our conceptions. If the contention be justifiable that the alterations attending dissolution are very largely alterations in the character of the water, attention has been directed of late far too exclusively to the dissolved substance.

To give emphasis to the view, I have advocated (*Roy. Soc. Proc.*, 1903, xxii., 80; *Science Progress*, Jan., 1909) the restriction of the name *water* to the liquid mixture and have proposed that the simple molecule represented by the symbol OH_2 be termed *Hydrone*. The generalised expression—



may be considered to be representative of the state of equilibrium in water—that is to say, of the character of the change which it undergoes when the conditions are varied either physically or by dissolving substances in it—in the sense that it pictures the resolution of the more complex into simpler forms and *vice versa*, without taking into account the variety of molecular forms ($x, x^1, x^2, \dots$) which are present.

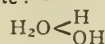
It is probable that the agreement between "theory" and practice on which reliance has been placed, particularly in interpreting osmotic phenomena, is more often than not only apparent and fictitious and but the outcome of counterbalancing effects which have been left out of account. We are too prone to believe in constants; we need to remember that, except perhaps in the case of the perfectly gaseous state, *constants are dependent variables*. To take an example, it is assumed that glucose and cane-sugar produce like osmotic effects when used in equivalent proportions; indeed, it has been the fashion of late years to treat non-electrolytes as harmless neutrals; in point of fact they differ as much in behaviour as do electrolytes, and such a conclusion must be viewed with the gravest suspicion. Recently Dr. Eyre and I have been able to show that three substances so similar as methylic, ethylic, and propylic alcohols produce effects in precipitating salts from solution which are markedly different, propylic alcohol being the most effective although the least soluble. It is clear that the precipitant does not act mainly by itself combining with and withdrawing water in direct competition with the salt; but that it promotes the *dissociation of water* by the mechanical interposition of its molecules; in fact, that the "dehydrating" powers of the *water* are enhanced owing to the increase in the proportion of simple molecules in the liquid conditioned by the presence of the solute.

The same effect is obvious when the reduction of the electric conductivity of a salt such as potassium chloride by equivalent quantities of the three alcohols is considered. This amounts to about 6 per cent in the case of methylic, 12 in that of ethylic, and 17 in that of propylic alcohol; the reduction effected by glucose, however, amounts to about 27, and that effected by cane-sugar to no less than 42 per cent. In these two latter cases the amount of water actually withdrawn from the solution by the sugar is probably considerable, and the "mechanical effect" of the solute is therefore exercised in a more concentrated solution—more concentrated, that is to say, than those in which the alcohols act. If therefore solutions of glucose and cane-sugar of equivalent strength produce like osmotic effects, it is because unperceived compensating factors are at work in the solutions which in algebraic sum have the same aggregate influence.

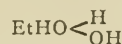
To explain the effect produced by substances which give rise to conducting solutions when dissolved in water (acids, alkalis, and salts), it is necessary to consider the special nature of the changes which may be supposed to attend dissolution in such cases. Why, it may be asked, is an aqueous solution of hydrogen chloride a conductor whilst that of alcohol is a non-conductor? I believe the answer to be that it is because, in the former case alone, the two components of the solution are *reciprocally distributed*; that it is because two correlative systems—



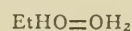
are produced which interact under the influence of the electric stress (see Note 6). In the case of alcohol no such interchange takes place. It may be that the alcohol is hydrolated to some slight extent, but the hydrol must be less basic than hydronol; probably, like ammonia, alcohol exists in solution for the most part in the hydronated state:—



Hydronol.



Ethanol-hydrol.



Ethanol-hydrone.

Much more must be learnt of the properties of solutions before definite decisions can be arrived at with regard to such delicate and refined issues.

I would apply the interpretation here given of the nature of conducting solutions generally to the explanation of all cases of chemical change; in other words, I assume that in all cases correlative systems are present which are formed by the reciprocal distribution of the interacting substances. From this point of view the solvent is no mere medium, but an active participant in the series of interchanges of which, as a rule, only the final product is noticeable.

The solution thus offered of the complex problem discussed very fully in my Address in 1885, which has ever since occupied my thoughts, will, I trust, be found to be helpful, although by no means complete in all its details.

In effect, the doctrine makes no demand which the chemist should not be able to grant forthwith, as it is generally supposed that hydrols are easily formed—to give an example, in the case of the conversion of chloral, CCl_3COH , into chloraldehydrol (chloral-hydrate), $\text{CCl}_3\text{CH}(\text{OH})_2$. The novelty of the conception lies in supposing that the occurrence of electrolysis involves the interaction of the hydrol and its correlative, and the explanation which it affords of the difference between electrolytes and non-electrolytes.

It is essentially an association theory, although it involves the dissociation of the interacting substances but never the production of separated ions. In the case of aqueous solutions the amount of the distributed substances may be taken as the measure of the activity—of the degree of ionisation, so-called. A wrong view prevails that the so-called molecular conductivities are measures of activity; they are in reality only measures of the relative activities under corresponding conditions of the substances to which they refer. The molecular conductivity of an acid is at a maximum in its weakest solutions; presumably it is then present to the maximum extent in its simplest state and in the active hydrolated state; but as a hydrolytic agent its activity is at a maximum near to the opposite end of the scale. In other words, the hydrolytic activities of a series of acids are in the order of their molecular conductivities in solutions of comparable strength, but molecular-hydrolytic and molecular-electrolytic activity run in opposite directions; the maximum electrolytic conductivity of an acid solution, which is manifest at a particular degree of concentration—presumably at the point at which the two forms of the distributed materials most nearly balance—is also in no way identical with maximum molecular hydrolytic activity. On these assumptions not a few of the deductions based on the ionic dissociation hypothesis are clearly fallacious.

It has been asserted that the association hypothesis does not admit of quantitative treatment, and that therefore it is at a disadvantage; but if the quantitative meaning given to various results in accordance with the tenets of the dissociation hypothesis be more often than not one which is inadmissible, little is gained by applying the speculation quantitatively. As already remarked, the only cases in which chemical and electrolytic activity can be compared by the methods proposed are those in which the comparison is made between solutions of comparable or equivalent strength—that is to say, between compounds arranged in vertical series in the order of their activity (see Note 7). Electrolytes are comparable in most, if not in all, their properties when the comparison is made in this way; but order of activity is one thing, actual activity another. It is in this sense, and this sense only, that we may agree with Arrhenius in his statement, "L'activité électrolytique se confond avec l'activité chimique."

The ionic dissociation hypothesis is a beautiful mare's-nest, which fails apparently to fit the facts whenever it is examined. "And the moral of that is," to quote the words of the classical Duchess so well known to children, "we must not use the words *ion* and *ionisation* in any speculative sense but confine their application to cases such as were contemplated by Faraday when he introduced the term *ion*; the conception of activity whether electrolytic or chemical, should alone be attached to such words; no idea of actual separate individual existence should enter into our minds in using them; the *ion* is to be thought of merely as the potentially active transferable radical in a compound, not as a separated particle enjoying independent existence." It is so easy to speak of dissociation when it is desired to give expression to the idea; the first thing the scientific speaker or writer should guard against is ambiguity.

The subject of gaseous interchanges must not be left out of account, although it is impossible to do justice to it. Mendeleeff's contention that gaseous interchanges are usually bimolecular has been defended by Dixon and Larmor of late. But the facts must be faced. The almost inconceivable frequency of the molecular impacts must not be forgotten. The extraordinary attractive power of the hydrone molecule is also to be remembered—this would tend to promote the formation of aggregates with which the necessary third substance would every now and then form a bimolecular system—which, however, would in reality be at least trimolecular. The proportion of hydrone molecules in a dried gas has probably been underestimated—the density of hydrone being very low (9)—as no dehydrating agent can be supposed to remove all such molecules, or even nearly all; the hydrated substance must have a certain pressure of dissociation. Sir James Dewar's appears to be the only method which is in any way deserving of the epithet absolute; the results he has obtained with helium in a radiometer are strongly in favour of my view. Lastly, the gradual growth in velocity of the explosive wave up to the point of detonation as the compression becomes greater is clear indication that reduction in volume and increase of opportunity for the formation of systems of the proper degree of complexity is a matter of great consequence. Even the behaviour of cordite is significant, particularly the projection of unburnt rodlets of the material from the gun; apparently it is not decomposed by shock intramolecularly but is decomposed by heat into gases, which interact explosively.

(To be continued).

NOTES TO ABOVE.

1. The solid model of silica which Barlow and Pope have constructed has very remarkable attributes, in that the oxygen atoms appear to be uniformly related and in intercommunication throughout its mass; so that a mass of silica, whatever its size, may almost be regarded as a single molecular complex. A similar view may be taken of plastic metals such as those of the platinum group, gold, silver, and copper. Whether when rendered brittle by

association with small amounts of impurity these are resolved into simpler molecular complexes or whether the molecules merely become separated by substances which promote discontinuity and brittleness, it is impossible to say at present. The cause of hardness in mineral materials is, however, a question of no slight interest and importance. The property is strikingly exemplified in the diamond. It is difficult to understand the intense hardness of this material, on the assumption that the diamond is composed of paraffinoid carbon—that is to say, carbon with all its affinities satisfied. At present we appear to have no clue to the manner in which affinity acts in promoting the formation of such solids. But it is obvious that all solids are possessed of some degree of "surface affinity," as they not only grow when placed in solutions but determine the separation of solid from a solution at a degree of saturation which is often considerably below that at which the solution is actually saturated with the substance; and such surface affinity, moreover, is selective, as the determinative effect is exercised only upon the substance itself or substances isomorphous with it—although exception must be made in favour of water, which all surfaces appear to attract. Sir James Dewar's observations on the condensation of gases by charcoal at low temperatures afford most striking illustrations of surface affinity.

2. In naming the inert gas in air, which he ultimately termed *azotic gas*, having proposed the name *azote* for the element, Lavoisier had in view as alternatives the terms *alcaligen* and *nitrogen*. As there was no proof that the element was a constituent of alkalis other than ammonia, he rejected the former name on the ground that it might convey too broad an impression; in course of time the latter is become the popular name, except in France, where motives of piety have prevailed; but the French practice has been justified by the universal use of the term *azo* in connection with many nitrogen derivatives.

Had Lavoisier realised that the alkalis and basic oxides generally owe their basicity to oxygen as much as acids and acidic oxides generally owe their acidity to oxygen—the one being oxygen tempered by metal, the other oxygen tempered by non-metal—as the number of basic oxides far outweighs the number of acidic oxides, he might well have chosen the name *alcaligen* rather than oxygen. The choice he made was a particularly happy one and striking evidence of his genius and sense of euphony—for oxygen is *par excellence* the acid-forming element and is most truly called *sour-stuff*, the stuff of which sour things are made—for whatever the properties of the initial oxide of a series, as the proportion of oxygen is increased the acidic qualities are invariably strengthened.

The choice of a terminal connoting the elementary radicles which would be applicable generally and also acceptable is very difficult. If usage do not forbid change, probably our ears will decline to allow us to be systematic. The terminal *gen* is not applicable to many present names. In the interest of euphony, exception may be taken to the adoption of *ion* as a final syllable. In English ears most of the words with this ending have an ugly sound if pronounced so as to make it significant; moreover, our object is to secure a term which is applicable to the elementary material, whatever its state; the term *ion* is suggestive of a particular state—a state of chemical activity; and at present there is no agreement as to the nature of an *ion*. The terms atom, radicle (simple and compound), *ion*, and molecule now all have their separate meaning and value and are indispensable.

The only terminal which seems in any way likely to be generally satisfactory in use is the terminal *yl*, which is already applied to organic radicles; its use might well be extended to radicles generally.

I may add here that it is unfortunate that certain disturbers of the peace have advocated of late a reversion to the spelling *radical*, mainly on the ground that the term is of French origin and was thus spelt originally. But there is no reason to give a French spelling to a word when it becomes English; and the genius of our language is

against the proposal, apart from the fact that it introduces unnecessary confusion. We make clear distinction between *principal* and *principle*; it is most desirable, in like manner, to distinguish between *radical* and *radicle*; the latter is in harmony with *particle* and *participle*, and being suggestive of a rootlet, it is eminently significant. *Radical* is almost misleading, as a radical in these days is apparently one whose tendency is to go to extremes while contemplating the surface only instead of going to the root of things.

It would be to the advantage of students also if we were far more systematic in our use of formulæ as well as in matters of nomenclature. At present no proper distinction is made between empirical and molecular formulæ in the case of the elements. Notwithstanding that we acknowledge our indebtedness to Avogadro and to Canizzaro his prophet, it is still not unusual to find gaseous hydrogen represented by the symbol H and gaseous oxygen by the symbol O; the text-books generally pay little heed to such matters. We are far too careless of consequences in our teaching and do not sufficiently appreciate the value of system and ritual. If it were made the practice to represent molecular formulæ in some special manner—by Clarendon or thick type, for example—attention would then be called to the fact that in the majority of cases the substances used are of unknown molecular composition.

If a student see sodium chloride always represented as NaCl or, what is worse, in accordance with a growing evil custom, learn to speak of it as *En-ay-see-el*, it becomes difficult to persuade him that probably such a formula is a misleading expression—at all events, in no way the expression of known fact. Nothing could be worse than the tendency which is coming over us to speak of substances in terms of their formulæ instead of by name. It is difficult to understand what can be gained by referring, for example, to carbon dioxide as *Cee-oh-too*. Such vulgarisms and also the substitution of formulæ for written or printed names should be discountenanced on every possible occasion.

The reproach is not unfrequently levelled at us that scientific workers lack literary style and that they do not take sufficient pains in describing their work clearly and concisely—too often with justice. At all events, as the complaint has been made from the Chair at several recent anniversary meetings at the Royal Society, some notice should be taken of it. (Complaint is made even in Germany; compare von Lippmann, "Ueber den Stil in den deutschen chemischen Zeitschriften," *Chemiker Zeitung*, May 6, 1909, p. 489).

Solecisms are only too abundant in our literature. It is sheer carelessness to speak of compounds "adding" this or that, instead of saying that they combine with it; the statement that a substance "analyses" is inexcusable. The use of such expressions is proof that no thought has been exercised in writing.

An old writer has expressed an eternal truth in saying: "All soche Authors as be fullest of good matter and right judgement in doctrine be likewise always most proper in wordes, most apte in sentence, most plain and pure in uttering the same."

3. I may here put on record the opinion Lord Kelvin expressed on this question in a letter to me dated September 13, 1906:—

"Ever since, nearly four years ago, we heard of the hundred calories per hour given out by radium, I have had on my mind the question of some possible mechanism such as that which you suggest by which energy from surrounding matter (far or near) could automatically come into radium to supply the energy of the heat which it gives out. The more I think of the question the less I see of that possibility. At present I can see nothing else than that the energy given out is taken from a previously existing store of potential energy of repulsive force between separable constituents of radium.

"The 'disintegration of the radium atom' is wantonly nonsensical. It is nonsense very misleading and mysti-

fying to the general public, because, if what is at present called radium can be broken into parts, it is not an atom.

"'Energy of an atom' implies a thorough misunderstanding of the meaning of the word energy, which is capacity for doing work.

"I admire most sincerely and highly the energy of the workers in Radio-activity and the splendid experimental results which they have already got by resourceful and inventive experimental skill and laborious devotion. I feel sure that as things are going on we shall rapidly learn more and more of the real truth about radium."

4. In my opinion the experimental evidence is in no way satisfactory. It appears to me to be desirable that in studying the phenomena of electric discharge in gases and especially in vapours of complex substances, the horrible pitfalls should be taken into account with which the field of work is studded; unless every precaution to secure purity—precautions such as Baker and Dewar have taught us to use—be taken at every step, the conclusions based on all such observations must be open to grave doubt.

5. Compare *Chem. Soc. Trans.*, 1895, 1122; *Roy. Soc. Proc.*, 1886, xl., 268; 1902, lxx., 99; 1903, lxxii., 258; 1904, lxxiii., 537; 1906, lxxviii., 264; 1907, lxxix., 586; 1908, lxxxi., 80; *Science Progress*, April, 1909.

6. I would repeat the plea I put forward in 1885 that the use of the term hydrochloric acid as applied to hydrogen chloride is undesirable if not unjustifiable; the solution of the gas may be said to contain *chlorhydric acid*, $\text{HCl}(\text{OH}_2)_x$. From my point of view, oxygen is a constituent of all acids.

7. Solutions of acids and alkalis have maximum conducting power at certain relatively high degrees of concentration. Hydrolytic activity also increases steadily in the case of acids as the solution becomes more concentrated; whether it attains to a maximum, and whether this coincides with the conductivity maximum is uncertain at present; it is very difficult to decide this point experimentally, as the rate of change is so rapid in strong solution; moreover, the action takes another course in strong solutions, as compounds are formed by the interaction of the hydrolyte and hydrolist, so that two changes are superposed which cannot well be followed separately.

THE COLORIMETRIC DETERMINATION OF LEAD IN THE PRESENCE OF IRON,

WITH SOME NOTES ON THE PREPARATION OF LEAD-FREE REAGENTS BY CO-PRECIPITATION WITH FERRIC HYDROXIDE.

By JOHN M. WILKIE, B.Sc., A.I.C.

THE determination of minute traces of lead dates from the reading of Warington's paper (*Journ. Soc. Chem. Ind.*, 1893, 97). His work concerned itself with citric and tartaric acids, and showed that lead could be determined colorimetrically with considerable accuracy in alkaline solution, using ammonium sulphide as precipitant. He insisted on the fact that comparisons must be made between citrate or tartrate solutions, and not between one of these and water. To avoid interference due to iron, he advised that the "solution of tartaric or citric acid, made alkaline with ammonia, should be treated with a few drops of potassium cyanide and heated to near boiling."

This conversion of iron to soluble complex cyanides not affected by alkaline sulphide had been previously recommended by Teed (*Analyst*, 1892, 142) as follows:—"Iron does not at all interfere with the test. If an iron salt is added to lemonade, for instance, and made alkaline with ammonia, the iron is kept in solution by the tartaric acid, and on addition of the potassium cyanide is converted into potassium ferrocyanide or ferricyanide as the case may be.

To liquids not containing tartaric acid it is easy to add a little in the event of iron being present."

Teed apparently considered that the tartaric acid merely kept iron in solution, and he drew no distinction between ferrous and ferric iron. Citric acid also forms complexes with iron salts. Teed assumes that the complex does not hold the iron so firmly as to inhibit its complete conversion into ferrocyanide or ferricyanide. Experiments were made to see whether this was so, and also if small amounts of iron were so firmly held as not to react to alkaline sulphide in the absence of cyanide. The mode of testing was as follows:—12 grms. of tartaric acid (in the form of a stock solution, 2 cc. of which contains 1 grm. acid) were placed in a Nessler cylinder with 0.05 mgrm. metallic lead (in solution as nitrate: 1 cc. = 0.01 mgrm. of lead) and a slight excess of 0.880 ammonia, and the volume after cooling was adjusted to 50 cc. Five similar tests were prepared, to which were added, before the addition of ammonia, ferrous sulphate in amounts respectively equivalent to 0.00, 0.05, 0.10, 0.15, and 0.20 mgrm. of metallic iron.

The tints developed on adding 3 drops of a sodium sulphide solution to each were practically indistinguishable. Larger volumes of ferrous iron, however, developed colorations corresponding to much more lead than that actually present. Identical tests were next prepared, but to each of these was added 1 cc. of 10 per cent potassium cyanide after addition of the ammonia. The maximum amount of iron now coverable was about 1 mgrm. With citric acid similar results were obtained, but the tints in presence of iron were in all cases somewhat different from those obtained in the absence of iron.

When ferric iron was substituted for ferrous iron much more interesting results were obtained. Taking citric acid first, it was found that with the addition of as small an amount of ferric iron as 0.10 mgrm. a persistent yellow coloration was developed, which did not disappear on making alkaline with ammonia and adding potassium cyanide. Boiling the alkaline solution discharged the colour to some extent, but on adding sodium sulphide to the cooled solution the tint produced was quite yellow and not comparable with that produced by the same amount of lead (0.05 mgrm.) in the absence of iron. Tartaric acid behaved somewhat similarly, but the tints did not deviate so widely from the normal. That the colorimetric determination of lead in citric and tartaric acids was made impossible by such trifling amounts of ferric iron was so surprising that attention next was turned to inorganic salts. No work appears to have been published on the applicability of the alkaline sulphide method to solutions free from tartaric acid. Hill (*Chem. and Drug.*, 1905, i., 388; *Journ. Soc. Chem. Ind.*, 1905, 901), whilst rendering an important service by showing that lead-free standards in some cases were not absolutely essential, assumed that tartaric acid played no special part. Unmindful of the fact that ammonia quantitatively precipitates iron from its inorganic solutions, he determines lead in inorganic salts by adding sodium sulphide after addition of ammonia followed by potassium cyanide. He also deprecates heating with the potassium cyanide. He quotes an experiment, confirmed by myself, for ferric iron to show that in the presence of 0.05 mgrm. of iron the process thus simplified hopelessly breaks down—that is to say, the colour of the finely divided ferric hydroxide quite covers that due to the lead sulphide. Of course this difficulty could be removed by filtration through a close textured filter, but ferric hydroxide in quantity drags down with it any lead present in solution. The question now to be solved was whether ferric iron in amount proportionate to the lead normally occurring in pure chemicals had the same effect. The substances worked on were sodium chloride and potassium nitrate—both of which contained negligible amounts of lead (less than five parts per million) and still smaller amounts of iron. The mode of working was very similar to that already described.

Substance Taken : Sodium Chloride, 12 grms.

Ferric iron added. Mgrms.	Lead added. Mgrm.	Ratio of iron to lead.	Lead in filtered solution.
4.0	0.05	80 : 1	None
4.0	0.20	20 : 1	None
1.0	0.10	10 : 1	None
0.5	0.10	5 : 1	None

Substance Taken : Potassium Nitrate, 12 grms.

Ferric iron added. Mgrms.	Lead added. Mgrm.	Ratio of iron to lead.	Lead in filtered solution.
1.00	0.05	20 : 1	None
0.50	0.05	10 : 1	None
0.25	0.05	5 : 1	None
0.10	0.05	2 : 1	None
0.05	0.05	1 : 1	0.02 mgrm. approx.

Experiments 7, 8, and 9 were repeated by a colleague, except that the solution of potassium nitrate containing added iron and lead was cooled in each case before adding the ammonia and potassium cyanide. Precisely identical results were obtained. Experiments were next made to show that:—

1. Potassium cyanide plays no special part in the co-precipitation of lead by ferric hydroxide, bearing in mind that lead cyanide is an insoluble salt.

2. Subsequent heating with potassium cyanide has no appreciable solvent action.

3. The precipitation of lead is independent of a high salt concentration.

A mixture of 0.05 mgrm. lead and 0.10 mgrm. ferric iron, used in the forms already described, was diluted to a volume of 50 cc. with cold distilled water, excess of ammonia added, and the whole filtered through a close textured filter. No lead was found in the filtrate, thus supporting statements 1 and 3.

A similar experiment was next made in which 1 cc. of 10 per cent potassium cyanide solution was present, after excess of ammonia had been introduced, and the whole boiled several minutes. No visible diminution in the amount of the ferric hydroxide occurred, and the cooled filtrate showed no lead to sodium sulphide.

Experiments were made with magnesium sulphate as a type of salt of a metal having an insoluble hydroxide. Similar results were obtained, but to insure complete precipitation of lead about ten times as much iron must be added—limited amounts of ammonia being used.

The futility of professing to adopt Teed's process, while omitting tartaric acid, is thus demonstrated (*cf.*, an anonymous correspondent in the *Pharm. Journ.*, 1908, i., 181). The direct bearing of the above on the preparation of lead-free chemicals must not be overlooked—all that is necessary is to add a minute amount of a ferric salt (chloride), make distinctly alkaline with ammonia, and filter out the co-precipitated hydroxides. This process is now being used for the preparation of lead-free ammonium chloride. In this connection it has been puzzling to account for the fact that commercial salts, *e.g.*, ammonium chloride, sodium sulphate, &c., often show greater freedom from lead than the purer salts. In the light of the above the reason is obvious. It is also curious to reflect that the U.S. Pharmacopoeia recommends testing for heavy metals in ferrous sulphate by adding hydrogen sulphide to the filtrate obtained after precipitation of iron as ferric hydroxide.

Since in the presence of ferric iron Teed's process breaks down for citric and tartaric acids, and in the simplified process of Hill entire loss of lead may occur, it seemed best to now consider whether the method was inherently wrong or only in points of detail. For quantitative conversion to soluble complex cyanides it is obvious that precipitation of iron should take place in intimate contact with the potassium cyanide—and that if this were done the tartaric acid might be safely omitted. Preliminary experiments showed that an essential difference existed between ferrous and ferric iron. With the latter the solution always became coloured on treatment with potassium

cyanide—no matter for surprise considering the high tinctorial power of potassium ferricyanide. Consequently, the first series of experiments was performed with ferrous iron (ferrous sulphate). Brief consideration will show that intimate precipitation of ferrous hydroxide in the presence of potassium cyanide may be effected in one of two ways:—Either the acid solution of the iron salt may be added to the potassium cyanide or the potassium cyanide to the iron solution. If the acid is present in considerable excess the alkalinity of the potassium cyanide may be increased by addition of ammonia; in all cases the liquid must finally possess a strong alkaline reaction.

A solution of ferrous sulphate was made of which 5 cc. contained 1 mgrm. of ferrous iron and 0.2 cc. normal sulphuric acid. In one experiment 1 cc. of this solution was diluted to 40 cc., 1 cc. of 10 per cent potassium cyanide added slowly with constant rotation followed by 0.5 cc. 0.880 ammonia, and the colourless solution adjusted to 50 cc. On addition of sodium sulphide no colour was developed and the solution was practically water white. The experiment was repeated four times, adding 0.05 mgrm. lead in each case and 0.05, 0.10, 0.15, 0.20 mgrm. of ferrous iron respectively.

In all cases colourless solutions were obtained which on addition of sodium sulphide gave perfectly normal colorations. Ferrous iron in larger quantity was next added, viz.:—0.25, 0.50, 0.75, 1.0, 2.0, 3.0, 4.0 mgrms.

In all these the solution, after addition of the ammonia, had a slight colour, which disappeared on heating, but with amounts larger than 0.50 mgrm. it was found better to mix the ammonia with the cyanide before adding, as otherwise a certain amount of Prussian blue was formed.

To extend the method to ferric iron necessitates preliminary reduction to the ferrous condition. Any reducer selected must be efficient, easily obtainable, lead free, and not precipitable by alkaline sulphide. Sodium sulphite ($\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$) fulfils most of these requirements, and the mode of using is simplicity itself. 1 cc. of a saturated aqueous solution is added to the salt solution, to which has previously been added 4 drops 1.16 hydrochloric acid; heat is then applied until the colour due to ferric iron suddenly bleaches; to the colourless solution is added a mixture of 1 cc. 10 per cent potassium cyanide solution and 2 cc. 0.880 ammonia. The whole is again heated and gently boiled, if necessary, until quite colourless, cooled, and treated with sulphide in the usual manner.

The experiments detailed for ferrous iron were now repeated with ferric iron reduced with sodium sulphite as described. Solutions containing 0.05 mgrm. lead and 0.05, 0.25, 0.5, 0.75, 1.0, 2.0, 3.0, 4.0 mgrms. of ferric iron respectively gave quite colourless solutions, which on addition of sodium sulphide were indistinguishable from each other, and from solutions containing the same amount of lead (0.05 mgrm.) but no iron. The method thus modified worked satisfactorily in presence of the ordinary inorganic salts. Amongst others worked on were potassium, sodium, and magnesium sulphate, chloride, and nitrate, phosphoric acid and ammonium and sodium phosphates—the mode of working in all cases being to add 4 mgrms. of ferric iron to the maximum amount of any particular salt permitted by its solubility. In the case of salts like ammonium phosphate, for instance, a greatly increased amount of acid must be added to keep iron in solution—in this particular case 7.5 cc. of 1.16 hydrochloric acid was added to 12 gms. of the salt, a proportionately increased amount of ammonia being demanded.

In view of the extremely unsatisfactory results obtained with citric and tartaric acids these were again examined. It seemed not unlikely that here again better results would be obtained by adding the potassium cyanide direct to the solution of the acid, and not after previous neutralisation with ammonia, as from previous work it was thought that the iron would then be more reactive.

It was found possible to add several milligrams of ferrous iron just as satisfactorily as in the absence of

the organic acid. But in the case of ferric iron, the greatest difficulty was experienced in finding an effective reducing agent. Sodium sulphite failed to discharge the colour produced by ferric chloride in presence of citric acid. At last sodium thiosulphate was found to act perfectly. The actual details of one of the tests may be given here.

12 gms. of citric acid, 4 mgrms. of ferric iron, 0.05 mgrm. lead were placed in a Jena flask, and water added so as to give a volume of about 35 cc., 2 cc. of 1N/10 sodium thiosulphate was added, and the whole heated to incipient boiling and the flame removed. After about five minutes the solution became perfectly water-white, and to it was immediately added 1 cc. of 10 per cent potassium cyanide and then excess of 0.880 ammonia (13 cc.), and the whole gently boiled until colourless.

With tartaric acid the ammonia must be added in slight excess only, or a slightly coloured solution will be obtained even in the absence of appreciable amounts of iron.

Theoretically, 4 mgrms. of iron require 28 mgrms. of potassium cyanide for conversion to potassium ferrocyanide, whereas 100 mgrms. (about three and a-half times this amount) were regularly used. In one experiment, keeping the iron constant, the cyanide was cut down to one-half, and successful results were obtained if the cold acid ferrous solution was added to the potassium cyanide mixed with sufficient ammonia to give finally a distinctly ammoniacal solution. As considerable dexterity was required to obtain satisfactory results no further experiments were undertaken with amounts of cyanide nearer to theory. In fact, for convenient working the ratio of 25 to 1 should not be diminished. A few words may be added on the value of sodium thiosulphate in the reduction of iron for work of this kind. In my experience complete reduction occurs only in acid solution, but unlike sulphurous acid or sulphites the action is not retarded in the presence of large amounts of strong acids, &c. Its reducing action depends upon its conversion to tetrathionate in accordance with the following equation, which is practically quantitative under the prescribed conditions— $2\text{Na}_2\text{S}_2\text{O}_3 + 2\text{FeCl}_3 = \text{Na}_2\text{S}_4\text{O}_6 + 2\text{FeCl}_2 + 2\text{NaCl}$.

Thus an amount very little in excess of theory effects complete reduction, but considerable latitude in the amount added is given without precipitation of sulphur or lead sulphide occurring, provided the cyanide and ammonia be added successively as soon as the solution becomes colourless. A certain amount of this flexibility is possibly due to the solvent action of sodium tetrathionate on nascent sulphur. Its unique value in the presence of large amounts of citric and tartaric acids has been already referred to.

In conclusion, a number of problems concerning the availability of the alkaline sulphide method of colorimetrically determining lead in the presence of iron have been investigated. An essential difference has been shown to exist between ferrous and ferric iron, ferrous compounds alone being capable of conversion by potassium cyanide to colourless substances not affected by alkaline sulphide. Ferric hydroxide has the power of adsorbing lead; and with many salts if the proportion of iron exceeds twice the lead present, precipitation is complete and no lead is left in solution. This property of ferric hydroxide when available greatly simplifies the manufacture of lead-free chemicals. Teed's process requires radical modifications; ferric iron if present must be reduced to the ferrous condition, and precipitation of ferrous hydroxide must occur within the sphere of action of the potassium cyanide. It is only when these two essential conditions are attended to that the addition of tartaric acid becomes superfluous. Sodium thiosulphate possesses special features as a reducing agent in work of this kind.

The author desires to express his indebtedness to Messrs. Boots, Ltd., for the use of their laboratory, in which the work was carried out.—*Journal of the Society of Chemical Industry*, xxviii., No. 12.

CORRESPONDENCE.

MATHEMATICALLY HARMONISING THE
ELEMENTS.

To the Editor of the Chemical News.

SIR,—Not knowing, at the time of my last communication (CHEMICAL NEWS, vol. c., p. 37), that the introduction of the three inactive elements in the Periodic Table would improve it considerably in one particular, I now suggest its modification, pending of course the confirmation of the new values in question deduced mathematically.

If the elements be arranged in the order of their increasing atomic weights (as shown in Mendeleeff's "Chemistry," vol. ii.), in which the satellite 0.27 and inactive element 9.75 and the radium emanation 174.97, also inactive, are introduced, the following regularity is brought to light. Between the satellite and helium, one element, hydrogen, occurs. Between helium and the next inactive element (weight 9.75), two elements occur, namely, lithium and beryllium. (Nitrogen is excluded because it has been assumed that it is a combination of the first three inactive elements, and the satellite is here regarded as inactive). Between "9.75" (I propose for convenience to call this *Nitron* Nt) and neon, there are four elements; and between neon and argon the number is eight. Between argon and krypton the number is sixteen, and between krypton and xenon sixteen or seventeen elements occur. Likewise, the same number is to be found between xenon and the radium emanation.

It will be seen that the number of intervening elements of the first five groups are, 1, 2, 4, 8, and 16 exactly, which figures are in geometrical progression. It is useless to attempt to continue the observation beyond the radium emanation, since there are too many uncertain or undiscovered elements involved, as high values are approached. There would, however, in all probability be 9 groups, with possibly an odd element or so over.

Probably the "17th" elements—not necessarily the last ones—of the 6th and 7th groups, assuming this increased number, carry satellites. Since Urbain (CHEMICAL NEWS, c., 73) seems to regard neoytterbium as a mixture, and some of the other elements are uncertain, it is necessary to forego judgment as to the probable exact number of elements in the 6th and 7th groups. It is even possible that some common impurity, when eliminated, will reduce the number.

By paralleling the groups or sections, so that the inactive gases head each column, a periodic arrangement is effected when the elements are simply displaced downwards (the numerical order being preserved) so as to line up horizontally those chemically allied. Eight or nine gaps due to displacements are obtained. It is interesting to note that tellurium is out of place as usual, but the displacement of iodine to match bromine leaves a gap into which it would chemically fit. There are some irregularities in the vertical series between samarium and lutecium. The operation is very simple, and the table compares favourably with existing classifications.

The above appears to be in perfect harmony with my previous work, and is indeed helpful in fixing the number of elements in the table based on the curves. Doubtless fluorine belongs to curve No. 2, the end columns taking only 6 elements. Probably bromine and gallium should stand in the centre. The first tabular group is thus rendered perfectly symmetrical and otherwise practically complete. As regards the second group, chromium has already been assigned to curve No. 12. Here also the end columns should probably take 6 elements each. There should therefore be only one gap on curve No. 18, and the remaining gaps are just sufficient to complete the full quota indicated by the series above.

It would appear from the 9 groups of the series that there are in all about 106 elements, and that the third

tabular group, based on the curves, would therefore be expected to take 31 or 32 elements as in the first similar group.

I take this opportunity of correcting a statement on page 39 (*loc. cit.*) which reads—"It seems more probable that an element, &c." It should read—"It seems more than probable that an element," &c.—I am, &c.,

F. H. LORING.

7, Doughty Street, London, W.C.,
August 20, 1909.

MISCELLANEOUS.

The Iron and Steel Institute—London Meeting.—In accordance with previous announcements, arrangements have been made to hold the Autumn Meeting of the Iron and Steel Institute in London on Monday, Tuesday, Wednesday, and Thursday, September 27th, 28th, 29th, and 30th, and Friday, October 1st, 1909. The following papers have been offered for reading:—

"Determination of the Power Consumption of Reversing Rolling-Mills," by C. A. Ablett (London).

"Comparative Tests of Cast Iron," by E. Adamson (Sheffield).

"Artificial Magnetic Oxide of Iron," by F. J. R. Carulla (Derby).

"Action of Air and Steam on Pure Iron," by J. Newton Friend, Ph.D. (Darlington).

"Corrosion of Iron," by J. Newton Friend, Ph.D. (Darlington).

"Uniform Moisture in Blast," by Greville Jones (Middlesbrough).

"Refining of Steel by Electricity," by Disponent E. J. Ljungberg (Falun, Sweden).

"Fuel Economy of Dry Blast, as indicated by Calculations from Empirical Data," by R. S. Moore (London).

"Growth" of Cast Irons after Repeated Heatings," by Professor H. F. Rugan (Tulane University, New Orleans, U.S.A.), and Dr. H. C. H. Carpenter, M.A. (Manchester).

"Maintenance and Renewal of Permanent Way," by R. Price-Williams (London).

"Constitution of Carbon-tungsten Steels," by T. Swinden, B.Met. (Sheffield).

Members who intend to take part in the discussions will, on notification of such intention to the Secretary, have copies of the papers forwarded to them a week in advance of the Meeting. For the completion of arrangements it is absolutely necessary that the number of members taking part in the various excursions, and the number of ladies accompanying them, should be known at once. Privileges in connection with the Meeting are personal and not transferable. Detailed official programmes can be obtained from the Secretary, Mr. G. C. LLOYD, 28, Victoria Street, London, S.W.

Soluble Starch.—Ch. Tanret.—The author's investigations show that the soluble starch, prepared by Fernbach's method, is a mixture of substances differing in rotatory power, in their reducing action on Fehling's solution, the coloration they give with iodine, and their solubility in alcohols of different strengths.—*Comptes Rendus*, cxlviii., No. 26.

NOTES AND QUERIES.

* Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Calcium Cyanamide.—Can any reader advise me with regard to calcium cyanamide (lime nitrogen)? I have an interest in lime works, and if likely to be profitable should like to manufacture the new nitrogenous fertiliser.—G. T. G.

THE CHEMICAL NEWS.

VOL. C., No. 2598.

ADDRESS TO THE CHEMICAL SECTION OF THE BRITISH ASSOCIATION.

WINNIPEG, 1909.

By Prof. H. E. ARMSTRONG, Ph.D., LL.D., F.R.S.,
President of the Section.

(Concluded from p. 117).

HAVING dealt with the subjects of chemical change and the nature of solutions, however inadequately, I must now endeavour to justify my opening reference to the importance of the organic side of our science.

The province of organic chemistry is so vast that it may appear to be difficult to distinguish the main lines of advance from the by-paths which intersect the field of inquiry in every direction. In reality this is not the case; certain salient features stand out which must attract attention if once attention be drawn to them. The efforts of the chemist to elucidate structure and to correlate structure with function have been extraordinarily successful. In the first place, as already remarked, the student of the subject now has his attention concentrated on the tetrahedron as the symbol of the *functional activity* of carbon; however numerous the compounds, he knows that certain simple rules can be laid down as applicable to all. It is established beyond question that carbon atoms have a remarkable tendency to form ring systems. The affinities of the atom seem to act almost rigidly in certain directions, which appear to be those of lines drawn from the middle point of a regular tetrahedron to its angular points. Rings containing either five or six atoms of carbon are therefore those which are most readily formed and of maximum stability; carbon atoms may and do unite in pairs, threes, and fours, but compounds of this order are far less permanent than those containing either five or six atoms, as the affinities appear to meet in such a manner that they do not satisfy each other, and consequently the compounds enter somewhat readily into combination with other substances. When the number of carbon atoms exceed six, not only is there less tendency to form a ring system, but the stability of the system is slight; when the number is considerable, stability is attained by the formation of complex systems, consisting of several rings conjoined (camphor, naphthalene, anthracene, &c.).

The behaviour of carbon compounds generally, in so far as this may be regarded as dependent on the condition of the carbon, is extraordinarily simple, and may be summed up in the statement that it is either paraffinoid, ethenoid, or benzenoid (see Note 8). Paraffinoid carbon is incapable of combining with other substances and but slightly attractive, so that the hydrogen atoms are by no means easily displaced from paraffinoid compounds (see Note 9); ethenoid carbon combines readily with various substances, forming compounds of paraffinoid type; in the benzenoid state, carbon appears to combine somewhat readily with a variety of substances, but the products enjoy only an ephemeral existence, and usually escape notice, as they at once break down, giving rise to benzenoid substitution derivatives, so that in this last form carbon simulates the paraffinoid state, but is more active.

In earlier years our attention was concentrated on benzene and the benzenoid compounds; much was done to elucidate the structure of these hydrocarbons and of their derivatives; meanwhile, these latter have proved to be of extraordinary significance technically, notably as dye-stuffs, but also on account of their medicinal value, as perfumes and in photography.

The structure of benzene has been the subject of much discussion during the period under consideration. I trust I shall not be accused of parental bias if I urge that the centric (see Note 10) formula is the best expression of the *functional activity* of the hydrocarbon benzene and its immediate derivatives; the attempts which have been made of late years to ruscitate the Kekulé oscillation hypothesis in one form or another appear to me to be devoid of practical significance. Any formula which represents benzene as an ethenoid must be regarded as contrary to fact. But in considering the properties of benzenoid compounds generally, it is necessary to make use of the Kekulé conception as well as the centric expression. The model of benzene devised by Barlow and Pope subserves a somewhat different and complementary purpose, being primarily of importance on the geometric side in discussing the relation of form to structure (see Note 11).

The discovery of trimethylene by Freund and the subsequent introduction of synthetical methods of preparing polymethylenes by W. H. Perkin, jun., mark the onset of a new era, opening out as they did the possibility of understanding the structure of camphor and the terpenes and other constituents of the volatile oils from plants.

Chemist after chemist had attempted in vain to solve the riddle presented by camphor. Suddenly, in a moment of inspiration, a satisfactory solution of the problem was offered by Bredt. The acceptance of the bridged ring, the special feature of the Bredt formula of camphor, marks the introduction of a new moment into organic chemistry.

The recognition of similar rings in several hydrocarbons of the terpene class, mainly in consequence of the masterly work of von Baeyer, has contributed in no slight degree to an understanding of these compounds; nevertheless, much remains to be learnt, and there are many and serious difficulties to be overcome before we shall be in a position to appreciate the genetic relationship of all the substances included in the group. When the account of the work is written it will form one of the most striking and fascinating chapters in the history of our science.

Among the many names of those who have contributed to its development the first to be mentioned is that of Wallach, to whose unwearied efforts, continued during a long series of years, so much is owing. The synthetic work carried out with brilliant success in recent years by W. H. Perkin may also be referred to as of extraordinary promise but of well-nigh inconceivable difficulty.

Before leaving this chapter reference should be made to the almost protean character of camphor, as disclosed by the work of inquirers such as Kipping, Pope, Forster, Lapworth, and Lowry; no other substance has lent itself to use in quite so many directions and with such fruitful results. Special mention may be made of the demonstration which Pope has given, with the aid of the camphor-sulphonic acids, that nitrogen, sulphur, selenium, and tin give rise to optically active substances in all respects analogous to those furnished by carbon. The success with which Kipping's arduous labours have been crowned is also very noteworthy, taking into account the many difficulties he has overcome in preparing optically active silicon compounds. The extension of the Pasteur-van't Hoff theory of asymmetry inferentially to all elements which are at least quadrivalent, now accomplished, is of superlative importance.

Lowry's refined observations on the conditions which determine the interconversion of isodynamic forms of some of the camphor derivatives may also be cited as of special value as a contribution to the study of metamorphism and the conditions which determine chemical change generally.

Not the least interesting feature of camphor is the light thrown by its behaviour on the influence which oxygen exercises as an attractive element, and on the part which spatial configuration may play in determining directions of change. It is clear that, whatever the agent, the attack is always delivered from the oxygen centre, and that the

direction in which the attack becomes effective depends on the position which the agent can take up relatively to the various sections of the molecule (*cf. Chem. Soc. Trans.*).

It must be confessed that our efforts to penetrate behind the veil in the case of the higher carbohydrates—starch and cellulose in particular—have not been rewarded with success.

Moreover, though much has been done of late years to unravel the nature of the *vegeto-alkaloids*, substances such as quinine are still only partially deciphered, and not one of the more complex alkaloids has been produced synthetically. In view of the fact that quinine is still the one effective and practically safe anti-malarial medicine, the disclosure of its constitution is much to be desired. The isolation of adrenaline from the suprarenal capsule and the discovery that this alkaloid—which is an extraordinarily active substance physiologically—plays a most important part in controlling vital processes is of supreme interest. Other glands—the pituitary gland, for example—appear to contain peculiar active substances, which are of particular consequence in regulating animal functions. The discovery of such substances affords clear proof that life is largely dependent on what may be termed chemical control.

In addition to indigo, the simpler yellow and red natural colouring matters have now been thoroughly examined, but this class of substance still affords abundant opportunity to investigators. Kostanecki's comprehensive studies of the xanthone group may be referred to as of particular value.

Attention may be directed here to the investigation of *brazilin* and *hæmatoxylin* by W. H. Perkin and his various co-workers, not merely as being full of interest and importance as a contribution to our knowledge of the relation between colour and structure, and as a brilliant example of technical skill, but because of the illustration it affords of the extreme intricacy of such inquiries and of the vast amount of labour they entail. The general public probably has not the slightest conception of the difficulties which attend such research work and of its costliness.

As an investigator of vegetable colouring matters, no one has been more assiduous or has displayed greater skill of late years than A. G. Perkin. His recent refined investigation of the colour-yielding constituents of the indigo plant is of exceptional value at the present time, although it is to be feared that it comes too late to save the situation in India. The work of the brothers Perkin, it may be pointed out, is of exceptional interest on the human side as well as from the scientific standpoint, as their enthusiasm and wonderful manipulative skill afford a striking and noteworthy example of hereditary genius.

Two substances of commanding interest which have long resisted attack—the red colouring matter of the blood and leaf-green—are at last going the way of all things chemical, as the secret of their nature is being wrung from them. In Willstätter's skilful hands *chlorophyll* is proving to be by no means the fugitive material it was supposed to be; the complexity of the problem it offers, however, seems to be far beyond anything that could have been anticipated; so much greater will be the interest attaching to the final solution. The discovery that green *chlorophyll* is a magnesium salt is of special importance, as the first clear indication of the manner in which magnesium salts are of service to plants.

Apart from the special interest which attaches to the investigation of vegetable colouring matters on account of their being coloured substances, such inquiries are of value as furnishing material for the discussion of the metabolic activity of plants (see Note 12).

Even colloids are being brought into line. Studded as they are with active centres (oxygen or nitrogen atoms), they seem to be able to attract and retain hydrone molecules at their surfaces in ways which give them their peculiar glue-like attributes; as a consequence living tissue appears to be little short of animated water.

To the present generation of students, the organo-

metallic compounds must have appeared to belong to the past; the discovery of methides of platinum and gold by Pope will not only serve to re-awaken interest in this group of compounds, but is of primary importance as a contribution to our knowledge of the valency of these elements; the stability of the platinum derivatives is altogether astonishing.

The discovery announced in June last, at the International Congress of Chemistry, by Mond of compounds of carbonic oxide with ruthenium and uranium is a striking and most welcome extension of his previous labours, which had placed us in possession of carbonyls of nickel, iron, and cobalt. The metallic carbonyls possess altogether remarkable properties; at present, these defy explanation; nickel carbonyl in particular seems to be an exception to all rules. The complex iron carbonyls made known by Dewar and Jones also have most fascinating attributes, the variety of colours they display being specially interesting. The marked individuality of the members of the iron group as exemplified in their carbonyl derivatives is in striking contrast with the tendency they display to behave as related elements; the deeper problems of valency are largely exposed for consideration in such peculiarities.

The discoveries of the special activity of magnesium as a synthetic agent and of the superior value of nickel as a catalyst in fixing hydrogen are other illustrations of the individuality of metallic elements. We are greatly indebted to the French chemists for the invaluable preparative methods they have based on the use of these two agents.

Although satisfactory progress has been made in almost every direction, many of the nitrogen compounds are still not properly understood. It is clear that we are as yet in no way seized with understanding of the attributes of this element as we are of those of oxygen and carbon, particularly in the case of mixed carbon-nitrogen compounds: we can make nothing of the physical data such substances afford. Nitrogen, in fact, is an extraordinary element, far more remarkable than any other; its "temper" appears to vary more than that of any other element according to the character of its associates—nothing could be more remarkable, for example, than the change in properties from ammonia, NH_3 , through hydrazine, NH_2NH_2 , to azoimide, N_3H . No other element can be so poisonous, so immediately fatal to life. We lack a model symbolic of its functions—which means that we are unable to fathom its vagaries and reduce them to simple order.

The oximes and the diazo-compounds in particular have given rise to much dispute. Stereo-chemical formulæ have been assigned to these, but probably they have little relation with the truth; although they have been of service by supplying symbols which can be offered up at examinations, by confining attention they have served to sterilise inquiry. No better illustration could be given of the truth of the remark made by my friend the Professor that man is an idolater by nature, a fact that chemists should always bear in mind.

The compounds in question are difficult substances to handle, far too prone to undergo change without invitation—it is to be feared that many of the conclusions which have been arrived at are based on incomplete if not unsatisfactory evidence (see Note 13). When I think of the state of our knowledge, I am reminded of the father of diazo-chemistry, Peter Griess, and of his marvellous experimental gifts; there is great need of such a man to re-investigate the whole subject.

If we inquire as to the general effect of the increase of knowledge of organic compounds, it is clear that the lessons which emerge from all modern inquiries are such as to justify Larmor's remark that our conceptions of structure must be granted more than analogical significance. Everything tends to show that function and structure are most closely connected—odour, taste, colour, physiological effect—are specific rather than general properties, each conditioned in its special variety by some special structure; we are approaching very closely to a time when it should

be possible to discuss such properties with considerable confidence.

Still it must not be forgotten that the problems they offer are all valency problems, and that the nature of valency eludes us entirely at present.

The greatest advance which chemists may pride themselves upon having made during the past decade or two remains to be considered. In 1885, I spoke as follows:—"The attention paid to the study of carbon compounds may be more than justified both by reference to the results obtained and to the nature of the work before us; the inorganic kingdom refuses any longer to yield up her secrets—new elements—except after severe compulsion; the organic kingdom, both animal and vegetable, stands ever ready before us. Little wonder, then, if problems directly bearing upon life prove the more attractive to the living. The physiologist complains that probably 95 per cent of the solid matters of living structures are pure unknowns to us, and that the fundamental chemical changes which occur during life are entirely enshrouded in mystery. It is in order that this may no longer be the case that the study of carbon compounds is being so vigorously prosecuted. Our weapons—the knowledge of synthetical processes and of chemical function—are now rapidly being sharpened, but we are yet far from ready for the attack."

My forecast has been more than justified; indeed, the advance to be recorded is nothing short of marvellous; the great problems of vital chemistry appear now no longer to be unattainable to our intelligence—their cryptic character seems to have disappeared almost suddenly. Many have contributed in greater or less degree, but none in such measure as Emil Fischer, whose work both in the sugar group and in connection with the albuminoids must for ever rank as monumental.

It is difficult to appreciate the extent to which the practical genius of this chemist has carried us—difficult alike for those who understand the subject and those who do not; the significance of his labours is only apparent when the bearing of his results on the interpretation of vital phenomena is fully considered. In 1885, we were disputing as to the structure of substances such as glucose and galactose; now, we not only are satisfied that they belong to the group of aldhexoses (aldoses) derived from normal hexane, but, taking into account the monumental discoveries of Pasteur, to which precision has been given by van't Hoff's great generalisation, we are in a position to assign fully resolved structural formulæ not only to the natural products, but to the nine other isomeric aldhexoses which Fischer has prepared artificially.

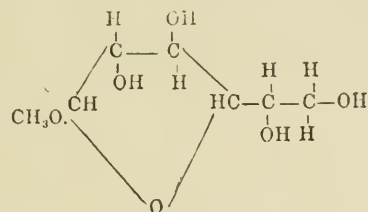
It is a striking fact that only three of the sixteen possible aldhexoses and but a single ketohexose (fructose), of which many are possible, are met with naturally. Nature is clearly most sparing, most economical, in her use of materials. And not only is this true of the hexoses, as very few of the possible lower and higher homologous carbohydrates occur in vegetable or animal materials, and the condensed carbohydrates (cane-sugar, starch, &c.), are all formed apparently from the hexoses and pentoses which occur naturally. The albuminoids, the alkaloids, the terpenes are also optically active substances; in other words, only a limited number of the possible forms are present. There is reason to suppose that the compounds of natural occurrence stand in close genetic connection, and belong with few exceptions to the same series of enantiomorphs; in no other way is it possible to account for the occurrence of one only of the pair of enantiomorphous isomerides and for the relatively small number of compounds. Moreover, not only the sugars and most of the other products of the disintegration of the albuminoids, but also the amino-acids, in like manner, are derivatives of compounds containing at most six atoms of carbon; the fats alone are of a considerably higher degree of complexity, but they are probably colloations of the simpler units.

The terpenes and essential oils are mostly C_{10} derivatives; the alkaloids have complex formulæ, but the units of

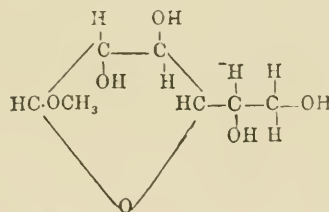
which they are composed are simple; as all of them are optically active, it is clear that only some of the possible enantiomorphous combinations are present.

We are bound, therefore, to assume that a large proportion of the changes which occur in living organisms—which constitute vital metabolism—are directed changes. What is the nature of the directive power? We are already able to go far in explaining this, although our knowledge is mainly of analytical changes, the nature of synthetic changes being, at present, only inferentially disclosed to us.

It has long been known that under natural conditions many complex compounds such as starch, cane-sugar, and other similar substances are broken down hydrolytically, not by the unassisted action of water but by the co-operation of enzymes; the effect produced by these enzymes is precisely similar to that of acids, except that all acids produce the effect, acting only with different degrees of readiness, whilst enzymes are strictly selective, a given enzyme acting only, as a rule, either on a single substance or on a series of substances similar in structure. Indisputable evidence has been obtained that the enzymes which act on the carbohydrates are intimately related in structure to the compounds which they attack, fitting them—to use the apt simile introduced by E. Fischer—much as a key fits into a good lock; the slightest alteration in the structure of the carbohydrate is sufficient to throw the enzyme out of action. The closeness of the association is well illustrated by the case of the two methylglucosides, which differ merely in the manner displayed by the following formulæ:—



α -Methylglucoside.



β -Methylglucoside.

The relative positions of the single hydrogen atom and of the hydroxyl group attached to the carbon atom are merely interchanged, but this is sufficient to render the one (the α) proof against the action of emulsin, the enzyme of the almond; the other (the β) proof against that of maltase, the enzyme present in yeast.

The enzyme may be pictured as attaching itself to a surface of the molecule and at the same time as associated with hydrone in such a manner that this is brought to bear at the junction which undergoes disruption. The action of acids, although similar, is simpler in that the attachment is not to the molecule as a whole, but only at, or near to, the junction which is resolved.

In the case of the albuminoids, the action is probably more local in character, in so far as the resolution of their polypeptide section is concerned, the same enzyme being able to effect the resolution of a considerable number of compounds.

All the peptolytes have in common the junction $C.CO.N$;

the peptoclasts by which such substances are gradually resolved probably fit this group alone; but other enzymes are of more complex organisation, akin to that of the sucroclasts—such as arginase, for example. In principle, however, the enzymes are to be regarded as all acting alike, each as fitting some particular asymmetric centre if not the whole of the molecule which undergoes hydrolytic disruption under its influence, the asymmetric centre being that at which the cleavage is effected.

In synthetic changes the operation is reversed. It may be supposed that the separation of hydrone is determined by the circumstance that water can be formed by the interaction of this hydrone as it separates with that which is attached to the hydrolated enzyme; the formation of water, in fact, plays a great part in such changes.

The action of oxydases may be regarded from a similar point of view. The early observations of Adrian Brown on the oxidising activity of *Bacterium Xylinum*, coupled with the later work of Bertrand, afford clear proof that these enzymes are possessed of selective powers. It is conceivable that such enzymes become attached to a molecule at some one centre, and that they then deliver their attack at some more or less distant point by presenting the oxygen with which they are loosely associated at this point. It is easy, on such an assumption, to understand how ethenoid linkages may be developed in various positions in the molecule of a fatty acid.

Rosenthaler's recent observations on the formation of optically active phenyl hydroxycyano methane, PhCH(OH)CN , from hydrogen cyanide and benzaldehyde on shaking the solution with emulsin are, however, among the most significant yet made. I have myself confirmed his statements. The ease with which the change takes place—the manner in which the change is accelerated by the enzyme—is altogether remarkable.

Although there can be little doubt, in the case of plants and animals, that the synthetic processes do not occur spontaneously and directly between the interagents, but are for the most part at some stage or other directed or controlled, it cannot well be supposed that every asymmetric compound is the direct outcome of a controlled process; nor is it necessary to assume that such is the case. Not a few asymmetric compounds are probably but secondary products formed by the breakdown of compounds which are the products of directed synthesis.

Ehrlich's observations on the formation of the amyl-alcohols from the isomeric aminocaproic acids (leucines) may be referred to in this connection. Taking into account the manner in which the vegetable organism is provided with conservative powers and its tendency to retain nitrogen, in view of the peculiar structure of the members of the terpene group—especially the presence of the isopropyl group and of methyl in association with the ring in such hydrocarbons—it is highly probable that the terpenes are derived from amino-acids. A molecule of leucine, a molecule of alanine, and a molecule of formaldehyde obviously provide the materials for the production of methylisopropyl-dihydrobenzene; it is not difficult to picture the series of changes which would lead to the formation of the hydrocarbon from such a conjunction.

The general impression produced by facts such as have been referred to is that directive influences are the paramount influences at work in building up living tissues. These come into operation, it is to be supposed, at a very early stage in the case of the plant. The initial step probably involves the electrolysis of water under the influence of solar energy and the reduction by the hydrogen thus liberated of the carbon dioxide, which is eventually converted into formaldehyde, either directly or, it may be, through the intermediation of oxalic and formic acids. The part which chlorophyll plays in this process can only be surmised; it is not improbable that reduced chlorophyll is the active reducing-agent; that chlorophyll itself is active in conditioning the resolution of water under the influence of solar energy into reduced chlorophyll and oxygen or, more probably, a labile peroxide, from which

oxygen is independently split off at a subsequent stage, it may be under the influence of a so-called catalase.

Whatever the process by which the plant acquires its initial store of carbonaceous material, the formaldehyde is apparently at once made use of, and in part at least converted into starch. The view may be taken that glucose is the primary product of condensation—that the formaldehyde molecules become ranged against a glucose template in series of sixes, which are soldered by enzymic influence into a single molecule by the interaction of contiguous hydrogen and hydroxyl radicles along the chain.

The glucose is thereafter carried a stage higher and converted into maltose, or it may be that a maltose template is effective from the beginning and that the biose is the immediate product of condensation; the conversion of maltose into starch must take place in some similar manner. The recent observation that cellulose is a β -glucoside enables us to realise that the formation of cellulose differs from that of starch in that the glucose molecule, instead of being converted into the β -glucoside maltose, becomes changed into the correlated β -glucoside, a membrane being thus secured which can resist the diastatic enzymes by which starch is attacked.

The formation of the albuminoid substances may be regarded from a similar point of view. At present, however, there is no satisfactory evidence to show at what stage nitrogen is introduced into the molecule. As the plant takes up nitrogen in the form of nitrate, not as ammonia, it is probable that the nitrate is reduced to hydroxylamine, and that this rather than ammonia is the active synthetic agent. Formaldehyde and hydroxylamine would yield formaldoxime, which would easily pass into methylamine on reduction; the interaction of formaldoxime and formaldehydrol might give rise to a higher aldoxime which would be easily convertible into aminoacetic acid (glycine). Higher glycines might be formed from glycine by syntheses similar to those Erlenmeyer has effected; but to account for the formation of asymmetric amino-acids it is necessary to assume that the action is controlled at this stage and that the glycine is formed against a template perhaps under the influence of an enzyme.

Another conceivable mode of formation is by the fermentative degradation of glucosamine.

Until we know more of the order in which the amino-acid radicles are united in the various albuminoids and of the character of the associations other than those which are characteristic of polypeptides, we can consider the formation of albuminoids only from a very general point of view; but taking into account the very different proportions in which amino-acids and other cleavage products are formed on hydrolysing substances of different origin, it is clear that the several sections of the molecule must be differently ordered in the different proteins; again, therefore, it is necessary to assume that the formation of such substances is directed. We may picture molecule after molecule as being "brought into line" against a template and the junctions which are required to bind the whole series together as being made through the agency of the enzymic dehydrating influence before referred to.

Attention has been called to the relatively simple way in which the hydrocarbons are constructed, that even the paraffins are not to be visualised as so many ducks strung upon a ramrod, Münchausen fashion, but as forming curls, owing to the natural set of the affinities. This probably is true of complex substances such as the proteins.

Protoplasm, in fact, may be pictured as made up of large numbers of curls, like a judge's wig—all in intercommunication through some centre, connected here and there perhaps also by lateral bonds of union. If such a point of view be accepted, it is possible to account for the occurrence in some sections of the complex series of interchanges which involve work being done upon the substances brought into interaction, the necessary energy being drawn from some other part of the complex where the interchanges involve a development of energy.

The conclusions thus arrived at may be utilised in

discussing the problem of heredity. The inheritance of parental qualities, the need to assume continuity of the germ plasm, and the comparative unimportance from the standpoint of heredity of somatic qualities, as well as the non-inheritance of mere environmental effects (acquired characters), are all necessary consequences of the view I have advanced.

The general similarity of structure throughout organised creation may well be conditioned primarily by properties inherent in the materials of which all living things are composed—of carbon, of oxygen, of nitrogen, of hydrogen, of phosphorus, of sulphur. At some early period, however, the possibilities became limited and directed processes became the order of the day. From that time onward the chemistry prevailing in organic nature became a far simpler chemistry than that of the laboratory; the possibilities were diminished, the certainties of a definite line of action were increased. How this came about it is impossible to say; mere accident may have led to it. Thus we may assume that some relatively simple asymmetric substance was produced by the fortuitous occurrence of a change under conditions such as obtain in our laboratories, and that consequently the enantiomorphous isomeric forms of equal opposite activity were produced in equal amount. We may suppose that a pool containing such material having been dried up dust of molecular fineness was dispersed; such dust falling into other similar pools near the crystallisation point may well have conditioned the separation of only one of the two isomeric forms present in the liquid. A separation having been once effected in this manner, assuming the substance to be one which could influence its own formation, one form rather than the other might have been produced. An active substance thus generated and selected out might then become the origin of a series of asymmetric syntheses. How the complicated series of changes which constitute life may have arisen we cannot even guess at present; but when we contemplate the inherent simplicity of chemical change and bear in mind that life seems but to depend on the simultaneous occurrence of a series of changes of a somewhat diverse order, it does not appear to be beyond the bounds of possibility to arrive at a broad understanding of the method of life. Nor are we likely to be misled into thinking that we can so arrange the conditions as to control and reproduce it; the series of lucky accidents which seem to be required for arrangements of such complexity to be entered upon is so infinitely great.

The ovum and the spermatozoon must be supposed to have all the directive influences stored up in them which are subsequently brought into play in the development of the organism; they may be looked upon as bundles of templates of very definite structure. As both paternal and maternal qualities may be handed on to the offspring, and as there is so near an equality of the sexes in the higher organisms, it appears likely that the male and female elements are produced in equal numbers by both parents, either the one or the other becoming developed at conception, according to the accidents of the moment, whereby both the sex of the offspring is determined and whether it be primarily derived from the one or the other parent.

There cannot well be complete interpenetration of the two elements; rather it is to be supposed that surface contacts are established which lead to transferences from one to the other chromosome; to use vulgar terms, that eyebrows are pencilled, the nose straightened, narrowed, or broadened, hair made fair or dark; that by interpenetration of the curls this or that other quality is modified by a molecule being plastered on here, another smoothed off there, while cross-connections are established in some directions but broken in others.

Such a picture cannot be regarded as extravagant. We may even claim literary appreciation in support of our temerity—no less a writer than Emerson, for example, as witness the following passage in his "Uses of Great Men"—

"Light and darkness, heat and cold, hunger and food, sweet and sour, solid, liquid and gas, circle us round in a wreath of pleasures and, by their agreeable quarrel, beguile the day of life. The eye repeats every day the first eulogy on things: 'He saw that they were good.' We know where to find them; and these performances are relished all the more after a little experience of the pretending races. We are entitled also to higher advantages. Something is wanting to science until it has been humanised. The table of logarithms is one thing and its vital play in botany, music, optics, and architecture another. There are advancements to numbers, anatomy, architecture, astronomy, little suspected at first, when, by union with intellect and will, they ascend into the life and reappear in conversation, character, and politics.

"But this comes later. We speak now only of our acquaintance with them in their own sphere and the way in which they seem to fascinate and draw to them some genius who occupies himself with one thing all his life long. The possibility of interpretation lies in the identity of the observer with the observed. Each material thing has its celestial side; has its translation, through humanity, into the spiritual and necessary sphere, where it plays a part as indestructible as any other. And to these their ends all things continually ascend. The gases gather to the solid firmament; the chemic lump arrives at the plant and grows; arrives at the quadruped and walks; arrives at the man and thinks. But also the constituency determines the vote of the representative. He is not only representative but participant. Like can only be known by like. The reason why he knows about them is that he is of them; he has just come out of nature or from being a part of that thing. Animated chlorine knows of chlorine and incarnate zinc of zinc. Their quality makes his career, and he can variously publish their virtues because they compose him. Man made of the dust of the world does not forget his origin; and all that is yet inanimate will one day speak and reason. Unpublished nature will have its whole secret told."

Our modern faith in the ultimate power of scientific inquiry to appreciate the precise character, if not to solve the most difficult of problems, is clearly leading us to seek in incarnate oxygen, in incarnate hydrogen, nitrogen, and a few other elements the secrets even of life itself.

We are undoubtedly what we are in virtue of the fact that carbon and hydrogen and oxygen and nitrogen are possessed of certain qualities—of qualities which permit them to take part in the formation of plastic and multi-mutable structures. No other elements apparently could lend themselves to the purpose; they would only furnish rigid structures; so that if there be life upon other worlds than ours it is probably not so very different from that with which we are acquainted (see Note 14). The uniformity of plan upon which the world of life is constructed is indeed remarkable. Obviously if the control were not a very rigid one, if possibilities of change were not strictly limited, the world would be full of abortions.

The manner in which development proceeds must depend (1) on the fundamental properties of the constituent primary units—that is to say, the elementary atoms; (2) on the structure of the germinal masses; (3) on the available primary food materials; and (4) on the character of the operative enzymes, whose work it is to incorporate into the protoplasmic complexes the scattered elements as they come into position on the various templates the nuclei afford.

It would seem that control is exercised and stability secured in several ways; not only is the form laid down in advance but certain chosen materials are alone available, and the builders can only unite particular materials in particular ways. Growth must depend on the presence of the necessary materials in great variety and in proper proportions. From this point of view the minor constituents of food are equally as important as the major constituents; the value of a varied as well as of a sufficient diet cannot be over-estimated, in fact. Yet it is probable that there is

a certain degree of equivalence, and that within limits one simple material may take the place of another; in any case, that growth may be favoured in this or that direction by the relative preponderance of a particular food material (see Note 15). It is conceivable that variation may arise by the accidental intrusion of a new structural unit into the complex; it is more probable, perhaps, that it is usually a consequence of growth in directions which, although possible, had not been favoured previously by the conditions.

But if such argument be sound, what are its consequences? Miss Barrington and Professor Karl Pearson conclude a recent communication from the Francis Galton Laboratory for National Eugenics with the words:—"The first thing is good stock, and the second thing is good stock, and the third thing is good stock, and when you have paid attention to these three things, fit environment will keep your material in good condition. No environment or educational grindstone is of service unless the tool to be ground is of genuine steel, of tough race, and tempered stock."

I will venture to assert that our chemical experience, especially our knowledge of enzymes, is in complete harmony with this conclusion.

Questions such as these are the questions of the future, and they are the questions that should be discussed by us at our meetings on account of their public importance. To repeat Emerson's words—something is wanting to science until it is humanised. The present is controlled by the past, and the present will control the future; the part played by education must be altogether subordinate, the provision of the right material to be educated must be the main consideration. Nothing could be worse than our present system; we place no hindrance in the way of the unfit, and those who are presumably the fittest are failing to contribute in proper proportion to the perpetuation of their race. The condition of affairs to-day affords a most striking exemplification of the slowness with which civilised nations are learning to appreciate the lessons of science.

Recently I attended the celebration at Cambridge of the fiftieth anniversary of the publication of Darwin's revolutionary work, "The Origin of Species," in which the famous doctrine of Evolution was developed. Men of distinction from all parts of the world were there, but not one word was said of the tremendous import to humanity of the message which Darwin delivered. What is even more startling, at Cambridge and, of course, equally at Oxford, it is in no way required of students either at entry or during their period of residence that they shall be sufficiently acquainted with Darwin's work to grasp its significance and its consequences; practically only the few who study biology become aware of it (see Note 16). And yet we never tire of preaching the value of classical learning and of history—the real history that counts and that training in scientific method which would tend to broaden and inform the mind are in no way thought of by the literary triflers who pretend to guide the destinies of our youth. Surely some effective means must be devised that will enable us to revolt without further delay against our unnatural and generally worthless system of school and university training.

No problem can compare in importance with that of the future of our race. To consider it is the one plain duty before us, and the need becomes daily a more urgent one. Not only do we encourage deterioration at the lower end of the scale of intelligence in the manner pointed out in the passage quoted from Darwin, we are now through our system of higher education courting failure also at the upper end. Herbert Spencer forcibly drew attention many years ago to the tendency which the development of individuality must have to depress fertility, and to the evil effects of severe mental labour on women especially. It has been stated that in the United States of America the higher education of girls has been proved to sterilise them. Many of us probably have experience within our own circle

of observation which would justify such a conclusion; there are so many ways in which education operates to retard marriage, even if it have no direct effect on the organism.

Even if man-stuff and woman-stuff be in no fundamental way different materials, there are essential differences between the sexes which must be taken into consideration. During the active period of her life the woman is subject at intervals to influences which do not affect the man; various excitants (so-called hormones) come into operation, and produce effects which are altogether remarkable; her mental condition is consequently in a state of continued flux. Cause and effect in these cases are undoubtedly chemical in their nature. The changes which attend puberty are probably brought about by the more or less sudden outpouring of peculiar secretions which direct metabolism into new and special channels. It is clear that mental states have an important influence on metabolism, and that if influences are brought to bear from which the organism has been exempt in the past, effects must be produced the nature of which it is impossible to predict; therefore the creation of new interests may well be a source of most serious danger. The most disquieting feature of the times is the revolt of women against their womanhood, and their claim to be on an equality with man and to compete with men in every way. There should be no question of equality raised; when comparison is made between complementary factors the question of equality does not and cannot come into consideration. It is clear that should the struggle arise—and it is to be feared that it is coming upon us—there can be but one issue: woman must fail, and in failing must carry man with her to destruction, for she will inevitably cease to exercise her specific womanly functions with effect, so delicate is the adjustment of her mechanism. The evolution of the two sexes has been on different lines, and different qualities have been developed in them; it is probable that the germinal differences are profound. And education cannot remove the difference; although education may condition functional disturbances, it must be powerless to modify the structure and mechanism. Man is in no way what he is to-day in virtue of the education he has received during a few generations past; the education of the race throughout time has been something entirely different from what is thought of now as education. "Nature, the dear old nurse," not man, has done the work by a severe and drastic process of selection—by picking out men capable of doing men's work, and by picking out women capable of doing women's work; she has constituted them helpmates, and has had no thought of their being so silly as to wish to get in one another's way; this is a state brought on by an artificial, unsuitable system of education.

The subject has been brought before the chemical world in England recently by the application of a number of women to be made Fellows of the Chemical Society. Many of us have resisted the application because we were unwilling to give any encouragement to the movement which is inevitably leading women to neglect their womanhood, which is in itself proof that they do not understand the relative capacities of the two sexes and the need there is of sharing the duties of life. If there be any truth in the doctrine of hereditary genius, the very women who have shown ability as chemists should be withdrawn from the temptation to become absorbed in the work, for fear of sacrificing their womanhood; they are those who should be regarded as chosen people, as destined to be the mothers of future chemists of ability. The argument is applicable generally; it is surely desirable in all cases of declared ability that the education of girls should be directed so as to produce not merely minimum disturbance of the woman's attributes and charms but full understanding of the unique position of responsibility she occupies in the scheme of life.

Questions such as I have raised are of the utmost importance as bearing on educational policy. Our ideas of educa-

tion are in almost as inchoate a state as they were in 1885. We have been led, it is true, to recognise that our scheme of popular elementary education is a terrible failure, that its whole tendency has been to emasculate our population; yet at the very time that we are making this discovery we are beginning to force our higher education along lines which experience shows must be ineffective—along literary lines. I should be the last to deny that there is an undercurrent of improvement perceptible, but this is directed only by sporadic influences and is in no way favoured by most of those in authority. We are still suffering at the hands of those who have been our persecutors in the past—the clerics, who control most of the schools and whose outlook is almost as narrow as it ever was. The saving grace of science has in no way entered into their souls—how can it? The universities make no attempt to secure their redemption. London of late years has even reversed the enlightened policy the University so long pursued, and has allowed Latin to figure as alternative to science, not as the complement of science.

Our Association seems to have little or no effect on the public conscience. And the explanation is not far to seek. Our interests are too special; we are all too much wrapped up in our own affairs; too inconsiderate to co-operate effectively. We forget or do not realise that, "Something is wanting in science until it has been humanised"; we make no attempt to organise our forces and make good the claim we put forward to be the possessors of superior knowledge. A complete change of attitude on our part is required; we need to play the part of propagandists. We are almost unknown as popular writers, and the days of popular lectures are past. Practically nothing is done to train the public mind, and school science is in no way effective.

To speak particularly of my own subject, it is impossible to rate chemistry at too high a value in Canada. The maintenance of the fertility of your fields, the proper utilisation of your vast mineral wealth, the purity of your food supplies (see Note 17) will depend mainly on the watchful care and skill of chemists; but the educational value of the subject may also be set very high. If properly taught in your schools, it will afford a means superior to all others, I believe, of training faculties which in these days should be developed in every responsible citizen. No other subject lends itself so effectively as a means of developing the experimental attitude of mind—the attitude of working with a clearly conceived purpose to a desired end, which is so necessary to success in these days; and if care be taken to inculcate habits of neatness and precision and of absolute truthfulness, if care be taken to teach what constitutes evidence, the moral value of such work is incalculable. But to be effective it must be done under proper conditions, systematically; the time devoted to the work must be adequate; I would even advocate that the subject be allowed to come before conventional geography and history and other unpractical subjects, assuming that the training is given in a practical way and with practical objects in view, not in the form of mere lessons learnt by rote; if taught in the form of mere didactic lessons it is as worthless as any other subject as mental discipline. Let me add that I would confine the teaching to a narrow range of problems, but make it very thorough with reference to these.

Five-and-twenty years ago I made my appearance as an advocate of what has been dubbed the heuristic method—the method which entails putting the learner in the attitude of inquirer, in training the pupil to inquire always into the meaning of what is learnt. I believe it to be in principle the only true method of learning. The idea has found favour almost generally, but the progress made in applying it has been slight—and this was to be expected, as teachers were few and far between who could carry the method into execution; moreover, so few teachers will allow their pupils to learn; they are too impatient, and insist on teaching them, and on doing the work of teacher and

learner—in fact, in these days, the learner is a rarity, examinations have almost destroyed the breed. If here you desire that your children shall grow up virile men and women with some honesty of purpose left in them, you will end and not mend a system which is sucking the very life-blood out of the youth in the mother country—you will insist that your children shall be taught little but learn much.

When studied as a special object, chemistry, in particular, is one of the subjects which must be worked at long and persistently—mere technical skill counts for so much, and so few seem to possess the ability to become skilful chemists; in no other science does the element of understanding and an indefinable power of appreciating the character of changes as they occur play so conspicuous a part—in no other science is the faculty of judgment more necessary. In practice, the chemist in works is constantly called upon to exercise his judgment—he is only too often called upon to judge from appearances of conditions which are deep-seated; he is everywhere the works physician, in fact. It is therefore necessary that he should be highly trained and thoroughly versed in the art of inquiry. The men who in my experience have been successful are those who have learnt to think for themselves, and who have been capable independent workers—sufficiently broad-minded and sufficiently practised in their art to be able to turn their attention in any desired direction; I should add that they have been men who have learnt to read a much neglected art. Much has been said and written of late on the subject of technical training which is of value as bringing out the various points of view; the problem is a very difficult one, owing to the great number of interests to be considered and more especially the very uneven and often inferior quality of the material to be trained. The great danger of specialised technical training is the tendency to make it too narrow. Success in practice depends not merely on knowledge of subject but also, if not mainly, on the possession of certain human qualities which are not usually developed in the technical school and which cannot be tested by examination—it is unnecessary to specify them. It is undeniable that in England for many years past chemistry has suffered from the recognised fact that there has been little money in it—parents have been led therefore to prefer other careers for their sons, and the subject has not secured its due proportion of intelligence and is suffering in consequence. Too many of those who have entered works have had neither the intelligence nor—to speak plainly—the presence and manners that are required to secure confidence. The presence of men of gentlemanly bearing and instincts who have received thorough training in science, is urgently needed at the present time in many of our manufacturing establishments, to take the place of foremen of the old type, who have learnt all they know in the works and whose conceptions necessarily lack breadth; it is almost impossible to convince such men that improvements are possible, too often they adopt a selfish attitude and advisedly retard progress. Another direction in which an approach of interests is required is between chemist and engineer. The latter has too long occupied a dominant position in many works, and in not a few cases has done his utmost to exclude the chemist, fearing his competition apparently. The gas industry perhaps affords the most striking illustration of the effects of such a policy; on the engineering side it has been carried to a high pitch of perfection, but on the chemical it has ever fallen, year after year, to a lower state; now the quality of coal-gas is such, especially since the withdrawal of the sulphur clauses from the Acts of Parliament by which the industry is regulated, that gas is almost unusable (see Note 18).

But the iron industry is an even more striking case. The appliances are wonderful examples of constructive skill, but the engineer is clearly nonplussed when he seeks to understand the processes he nominally controls; the chemist has been kept so closely confined to his bench in the laboratory that he has had no proper opportunity of

studying the processes of manufacture systematically. No systematic study of steel has yet been made! Considering the magnitude of the industry and its importance, our knowledge of the subject is phenomenally slight; what we do know of the relation of strength and structure to composition is due to the pioneer labours of the late distinguished Dr. Sorby, an amateur unconnected with the industry—and to a fruitful conjunction of the labours of engineers and chemists outside the works, who in self-protection have tested the materials before use.

In Germany the chemist and the engineer have been placed on an equality and required to work together, with results which are altogether satisfactory. We need to adopt a similar practice. Any attempt to fuse the two into one will meet with failure, I am persuaded; they are called upon to work from different points of view—they need to be in sympathy and to understand one another, but their work is complementary. I have watched engineering students closely during years past and am satisfied that, on the average, they represent a type of mind different from that of the chemist—the tendency of the one is to be constructive and of the other to be reflective; the analytical work done by the chemist in the laboratory is but the means to an end—in the same way that the work done by the engineer in the drawing office is. Our future engineers should study chemistry and chemists should study engineering, in order that they may understand one another and work together—not in order that they may supplant one another. The chemist has to some extent allowed himself to be pushed into the background—perhaps because the average chemist in the past has been too tame a person; moreover, being forced to work in his laboratory, he has had less opportunity of gaining freedom and breadth of outlook than the more fortunate engineer, whose work has carried him out into the world.

You will be wise in Canada if you take care to select no small number of your ablest students—young men of promise physically as well as intellectually—and train them as chemists. Of late years attention has been called from every side to the inconsiderate manner in which raw materials, especially coal, iron, and wood, are being used up in all civilised countries; it is difficult to interest the public in such a subject, as few can appreciate the consequences, owing to the general ignorance of science and to the existence of an optimistic belief in the power of scientific discovery. But nothing will compensate for the exhaustion of your coal and iron supplies. It is your bounden duty to economise these in every possible way. The chemist and engineer will be required to help you in effecting economies by improving present methods of treatment. But the further question arises whether it be not also your duty, here in Canada particularly, without loss of time, to effect still greater economies by utilising the vast stores of energy in your possession, in the form of uplifted water, which now run to waste. The Falls of Niagara are the most glorious and entrancing sight in the world I have witnessed next to the total eclipse of the sun, yet I question whether it be permissible to allow any part of their available energy to be dissipated—whether the claims of posterity do not forbid us to allow æsthetic considerations to prevail in such a case.

To conclude, I have treated my subject very widely and at times vaguely, having ranged over a great variety of subjects—somewhat from the point of view of modern opera, perhaps; indeed, I am willing to confess that I have been much influenced of late years by music and by the recognition of the obvious desire reflective musicians have shown to secure breadth of effect and harmonious development of all the elements which go to compose a dramatic situation. Chemistry touches the drama of life at every point; if ever we are to understand life and regulate our actions in accordance with understanding, it will be in no slight measure because we appreciate the lessons which chemistry alone affords,

NOTES TO ABOVE.

8. A fourth condition requiring recognition is that of the carbon in acetylene; at present the acetylene compounds are so few in number, however, that this form may be left out of account.

9. The displacement of the hydrogen associated with carbon is in all probability a secondary phenomenon; it is likely that this is true generally, and that hydrogen is never merely removed or attracted away, but always has its place taken by a radicle which becomes temporarily attached to the multivalent atom with which the hydrogen is associated.

10. I have discussed this matter somewhat fully in a recent essay, with reference to the nature of amorphous carbon in connection with the remarkable work of Sir James Dewar, on the absorption of gases by charcoal at low temperatures (*Journal of the Royal Institution*).

11. The time is now approaching when it will be possible to extend the study of benzenoid compounds beyond the formal and superficial stage; hitherto we have been content to develop the methods of preparing such substances, and to determine their number and their distinctive properties. Everything has to be learnt as to the exact character of the changes which attend their formation from the parent substance benzene, and as to the exact nature of their inter-relationship. The impression produced by benzene, in my mind, is that of an eminently plastic system capable of responding to every slight change that may be impressed upon it. Nothing is more remarkable than the difference between benzene and its homologues, so obvious in the extraordinary increase in activity which attends the introduction of hydrocarbon radicles in place of one or more hydrogen atoms. But such plasticity is not characteristic of benzene only; if the properties of benzene-sulphonic acid be contrasted with those of the various substituted benzene-sulphonic acids, it is clear that every variation meets with some response from the sulphonic group; what is still more remarkable, if the hydrogen in the hydroxylic group in the phenolsulphonic acids be displaced by other radicles, not only does the oxygen atom to which the radicle is attached seem to respond to the change, but the benzenoid system and the still more distant sulphonic system are also affected. It is well known that the physical constants are all variables in the case of benzenoid compounds. Perhaps the most remarkable confirmation of the view here advanced, however, is that afforded by the conclusion arrived at by Barlow and Pope that in the case of benzene derivatives, although the spheres of influence of the carbon and hydrogen atoms are relatively the same as in the parent compound, the spatial arrangement of the component spheres of atomic influence remaining practically unchanged, nevertheless the actual volumes of the spheres of influence of both carbon and hydrogen alter proportionally to the alteration in molecular volume. Thus they maintain that in the case of the conversion of benzene (molecular volume, 77.4) into tetrabromobenzene (molecular volume, 130.2), the volumes of the spheres of influence of both carbon and hydrogen expand in the ratio of 77.4:130.2. Such a conclusion is very noteworthy.

12. But a note of sadness pervades the story. The effect of learning to understand Nature always appears to be that we at once brush her aside when we have wrested from her the secrets which she has so long preserved inviolate. No sooner did we learn the nature of the madder colouring matters than we proceeded to prepare them artificially—thus putting an end to the cultivation of a valuable crop. Indigo is meeting with a like fate, a catastrophe which might well have been avoided had scientific assistance been called in at the proper time. Not content with making natural colouring matters, we set to work to outlive the rainbow in our laboratories, and the feminine world is decked with every variety of colour in consequence, although, unfortunately, our blends too often lack the beauty of those of truly natural origin, which

rarely, if ever, offend the eye. We congratulate ourselves on our cleverness in thus imitating Nature, but no idea of thrift possesses us; moreover, our attempts to imitate if not to undo her work are never direct, but are always made with her aid, with Nature's product—coal; we are no longer content to ride on horseback, but must rush through space, and instead of watching the birds fly seek to emulate them, but always with the aid of fuel won by Nature from the soil and air in days long past. Too much is being done in every direction to waste natural resources, too little to conserve them, too little to employ man in his proper place—as tiller of the soil. Here lies the chemist's opportunity. At no very distant date, perhaps, when petrol is exhausted, toll will be taken from the sun in the form of starch or sugar, and this will be converted into alcohol.

13. Since this was written, Thiele's discovery of "Azomethane," MeN:NMe , has been announced. This is described as being, in the solid state, a distinctly coloured, very pale yellow substance. There can be little if any doubt, therefore, that, as Robertson and I have argued, the colourless so-called syn- and anti-diazo-salts cannot possibly be compounds of the $-\text{N:N}-$ or diazene type; such compounds would all be at least yellow in colour.

14. It has been suggested by Lord Kelvin and others that life may have been conveyed to our earth by meteorites. The experiments made, with Sir James Dewar's assistance, by Dr. Macfadyen prove that micro-organisms are not killed, even when cooled to the temperature of liquid hydrogen, so that they might resist the cold of space. Arrhenius has suggested in his "Worlds in the Making" that organisms may be conveyed directly from planet to planet by the agency of radiation pressure. Such organisms would be subjected, however, not only to intense cold but also to the action of ultra-violet light. Sir James Dewar was good enough recently to allow me to witness experiments he has been making to ascertain the effect of subjecting organisms which survive exposure in liquid air to the radiation from a quartz-mercury-glow-lamp while cooled in liquid air. He finds that, under such conditions, the organisms no longer survive. It would seem, therefore, that we must be content to consider the origin of life in our own planet and not throw the responsibility back on one of greater age.

15. It is from this point of view and not on the ground of any measure of temporary success that the advocates both of a spare diet and of vegetable food alone must be judged; in all such cases we have to consider the influence on the race, not merely the immediate effects.

16. Warning is given by Darwin in simple but explicit terms in the following passage in his "Descent of Man":—"With savages, the weak in body or mind are soon eliminated, and those that survive commonly exhibit a vigorous state of health. We civilised men, on the other hand, do our utmost to check the process of elimination; we build asylums for the imbecile, the maimed, and the sick; we institute poor-laws, and our medical men exert the utmost skill to save the life of everyone to the last moment. There is reason to believe that vaccination has preserved thousands who from a weak constitution would formerly have succumbed to small-pox. Thus the weak members of civilised societies propagate their kind. No one who has attended to the breeding of domestic animals will doubt that this must be highly injurious to the race of man. It is surprising how soon a want of care or care wrongly directed leads to the degeneration of a domestic race; but excepting in the case of man himself, hardly anyone is so ignorant as to allow his worst animals to breed."

17. I should like to take this opportunity of saying that it is impossible to over-rate the public value of the great work which Dr. Wiley has undertaken in the United States in endeavouring to secure the supply of food free from

deleterious ingredients. At home we certainly need some one to preach a similar crusade and to free us from doctored infants' foods and the innumerable host of medicines by which even our fair fields are disfigured.

18. Had not chemists entirely unconnected with the industry vastly improved the methods of burning it, gas would long since have fallen into disuse. At last, when almost too late, the industry is taking some notice of our science. It needs reformation and reorganisation root and branch. That an industry should exist whose business it is to sell, as the primary product of manufacture, so minor a constituent of coal as the gas we burn is an anachronism. We should gain vastly in our cities if we burnt soft coke instead of smoke-yielding coal. Lastly, it is now imperative that none of the valuable constituents of coal should be wasted. Combining these three considerations, it is obviously desirable that, in future, all coal should be coked, and both gas and coke supplied to the public instead, whilst the valuable residuals are used in other ways. No improvement has been effected by municipalities who have taken over the supply of gas; in the public interest some of these might well initiate such a change as is here suggested.

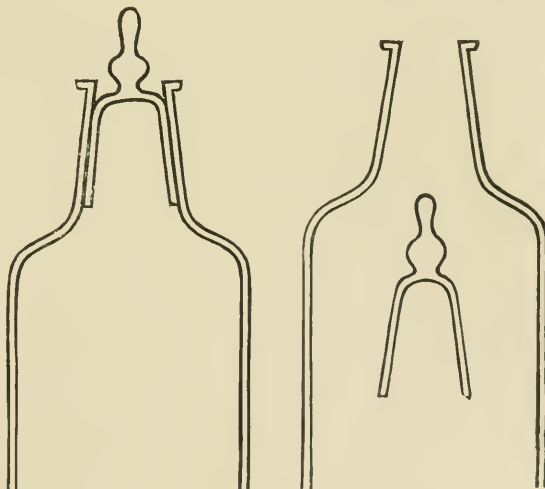
A SIMPLE METHOD FOR DETERMINING VAPOUR-DENSITIES AND FOR ANALYSING BINARY MIXTURES.

By PHILIP BLACKMAN.

Addenda.

1. THE author would be obliged if all those who feel interested enough to make enquiries concerning the method would kindly address their communications to Osborne House, 1, Osborne Street, London, E., in order to avoid delay in delivery and to ensure prompt despatch of replies.

2. It has already been pointed out that L and L_c are generally equal, or very nearly so, when experimenting with the glass-stoppered vessel. When inequality does occur, it is due to two causes: (a) the internal pressure is diminished by the action of "drawing outward" the



stopper to close the neck (for a similar reason the internal pressure in a flask is increased by "pushing inward" a stopper to close it); (b) while the vessel is being closed it has to be held in the hand, the warmth from which is sufficient to cause rise in temperature of the air within the apparatus, and on cooling again to t_1° the internal pressure consequently diminishes; both these effects result in the production of an increase of L to L_c .

3. It should be noticed that the apparatus supplied by Messrs. F. E. Becker and Co., Ltd., differs in one important particular (shown in the accompanying figure; and also, but not so clearly, in the figures in the *CHEMICAL NEWS*, vol. c., pp. 13 and 14) from the apparatus described in the *Zeit. Phys. Chem.* (1908, lxxiii., 639; 1909, lxx., 551) and the *Journ. Phys. Chem.* (1908, xii., 678; 1909, xiii., 427), viz., the lengths of the stopper and neck are such that when the former is drawn into the closing position its handle projects only partially outside the neck, so that when it is tied by thread to the neck there is no chance of its slipping back.

4. The thread should be fixed on to the handle of the stopper before the manometer and weighing-bottle are placed within the apparatus. It is easiest to make a small loop in the thread, which is dropped over the handle and the ends pulled tight.

5. The capillary tubing employed for the manometer should not be of too great a wall thickness, as otherwise time may be wasted in waiting for it to assume throughout the heating temperature.

6. If for any reason difficulty be found in getting the manometer past the stopper, then the stopper must be moved past the manometer, thus:—The stopper is lowered by means of the thread to the bottom of the apparatus, the manometer is put in so that it lies along the wall, and the stopper pulled up into position.

Errata.

At p. 14, line 43, instead of "be w ," read "be w_1 ." Line 47, in the formula, instead of " $(100 - w_1)$ " read " $(100 - w_1)$."

In the footnote (p. 13) add the reference "*Journal of Physical Chemistry*, 1909, xiii., 426."

Hackney Technical Institute, London, N.E.

ANALYSIS OF THE FRUIT OF A ROSE.

By LAYTON GOULDIN.

THE rose fruit used in this analysis was gathered near Mount Vernon, Iowa, U.S.A., October 19, 1907, from a rosebush eight years old and growing on black loam soil with a clay subsoil. The rose was one so crossed that it could not be assigned to any particular species. The fruit was thoroughly dry when work was begun on it. It had dried as a raisin, with similar creases and wrinkles, but, unlike the raisin, was hard, almost brittle, when crushing was attempted. The colour was a dark brown, nearly black, and the berry varied from one-half to one inch in length, and from one and a-half to two inches in circumference the short way. As mentioned before, the berry had a hard and brittle exterior, under which was a soft inner coat, not quite dry, enclosing a cavity containing a little brown fuzzy growth, in which nestled from one to three seeds of an irregular shape, not unlike wrinkled apple seeds, but shorter and a light brown, almost a tan in colour. When burned the first odour noticed was that of damp leaves. The smell after boiling a portion of the berries was of old coffee grounds, and the taste of a berry which was not quite dry like that of *candied lemon peel*, the sweetish and sour taste being noticeable together. Several portions of about 3 grms. each were ashed, giving 3.84 per cent of ash. Analyses were made for the following:—Silica, iron, alumina, magnesia, calcium sulphates, phosphates, sodium, potassium, manganese, and chromium. The results are shown in the accompanying table.

The separations used in dolomite analysis are those outlined in "Knight's Quantitative Analysis," and this work was also followed in determining the phosphates and sulphates. The alkalis were determined by an adaptation of J. Lawrence Smith's method of separation, and the manganese and chromium were determined volumetrically.

K ₂ O	..	..	..	..	12.81	per cent.
Na ₂ O	..	..	..	..	7.07	"
Fe ₂ O ₃	..	..	..	..	1.09	"
Al ₂ O ₃	..	..	..	..	24.01	"
MgSO ₄	..	..	..	..	5.91	"
SiO ₂	..	..	..	..	0.00	"
MgCO ₃	..	..	..	..	13.50	"
CaCO ₃	..	..	..	..	32.27	"
MnO	..	..	..	..	0.32	"
CrO	..	..	..	..	0.0005	"
P ₂ O ₅	..	..	..	..	2.25	"
Total..	..	..	..	..	99.1305	"

Manganese and Chromium.—These elements have never been noted before in fruits by any one in the laboratories, and their presence was first suspected when a slight green tinge was noted in several portions when they were ashed. From this it was reasoned that this colour resulted from manganese or chromium, or both, fusing with the alkali present during the process of ashing. Accordingly, after some of the berries were ashed, the ash was dissolved in concentrated HNO₃, a solution of AgNO₃ added with a few crystals of K₂S₂O₈, and heat applied. Immediately a wine colour appeared, indicating manganese. The solution was cooled to 30 degrees centigrade, H₂O₂ added, and one inch of ether. A bluish tinge showed through this solution, and after standing seventy-two hours the ether had collected this colour into a narrow purplish blue ring at the juncture of the ether and the solution, thus indicating the presence of chromium.

Chromium was tested for because it is a companion of manganese, and it was thought might be present, although there had not been any previous indication that there was any chromium in the berries. Afterward 4.1738 grms. of the berries were ashed, dissolved in 15 cc. HNO₃, AgNO₃, and K₂S₂O₈ added, and the solution was heated. The resulting wine colour was compared with tubes similarly prepared except no ash had been added, but instead had been treated with varying portions of a KMnO₄ solution, the strength of which was 0.000158 grms. to the centimetre. The original colour agreed with the tube containing 6.5 cc. of the KMnO₄ solution. From this the amount of manganese was determined. The original solution was then treated with a new amount of H₂O₂ and the blue tinge obtained thereby compared with tubes of a new addition of a solution of K₂Cr₂O₇ with a strength of 0.00000735 to a centimetre. By this method no difficulty was encountered in determining the amount of manganese and chromium present, although there was an infinitesimal quantity.

Ammonia.—When some of the berries were heated with soda-lime, a distinct odour of ammonia was present. This led to a test for proteins and a determination of the nitrogen.

Proteins.—The test with a dilute solution of CuSO₄ gave a blue precipitate, indicating albumin; also Mellon's reagent showed albumin, giving brick-red precipitate after the addition of a portion of a solution of the berries prepared thus:—12 grms. of the crushed berries were boiled in 400 cc. of water till the volume of the water was half the original amount. The solution was then filtered, and the filtrate used for the above protein test. The water smelled like baked squash, and the boiled berries gave the same odour; on putting some of the berries into the mouth this odour was again found to be present, and so strongly that it could not be confounded with anything else.

Nitrogen.—The nitrogen present was determined by the Kjeldahl method. 3.1131 grms. of berries were boiled in a round bottom flask with 25 cc. concentrated H₂SO₄ for thirty-nine hours. The liquid was removed to a casserole and diluted with water to 250 cc. Then KOH solution was added to strong alkalinity, using phenolphthalein as an indicator. After cooling thoroughly the solution was filtered, and two-thirds of the same distilled into a beaker containing 25 cc. of normal HCl, then titrated with normal NaOH, giving 0.643 per cent.

Sugars.—200 grms. of the fruit were put in a litre flask, the flask was nearly filled with 95 per cent alcohol, and placed upon a water-bath under a return condenser. Every twenty-four hours the alcohol was removed and fresh alcohol placed in the flask, and extracting continued. The alcohol that was taken from the flask was distilled off, leaving a residue which contained the sugars and acid, and which had a syrupy consistency, a dark reddish brown colour, and an odour of over-cooked sugar and molasses. This odour became less marked in the residual liquid as extraction continued. Occasionally some of the alcoholic solution was evaporated to dryness, dissolved in water, and tested with Fehling's solution. After 265 hours of treatment with alcohol the sugars were exhausted, the fruit was taken from the flask, dried at 125° C., and weighed. There were 115 grms. left, showing a loss of 85 grms. or 42.5 per cent sugar extract. The inside of the fruit was found to be softened by the treatment, but the exterior and seed remained hard. There were 468 cc. of the alcoholic extract. One centimetre of this solution diluted to 50 cm. of water reduced 18 cm. of Fehling's solution, which had a strength of 0.005 gm. On computation this showed 42.12 per cent of sugar, which agreed favourably with the percentage lost by weight. 50 cm. of the original alcoholic solution were diluted with water and digested with bone-black in a casserole. When the bone-black was filtered off very little colour remained, and the solution was evaporated to syrup, which had the appearance and taste of common corn syrup. Six portions of this syrup were treated with phenylhydrazine hydrochloride to obtain the osazone precipitates. These precipitates began to form in from fifteen to twenty seconds, and ceased to form in forty to forty-five seconds. According to Mulliken (*Journ. Am. Chem. Soc.*, May, 1906, p. 629), this indicates fructose. The osazone precipitates were treated with hot alcohol, and the filtered solution evaporated to crystallisation. Some inorganic impurities present in the crystals prevented the melting-point being determined, and after much labour this was given up. However, Wiley's colour test was tried on some of the syrup too. To some of the syrup some 5 per cent $\text{CO}(\text{NO}_3)_2$ solution was added, and some 50 per cent solution of NaOH. The colour reaction indicated dextrose. Afterward maltose and lactose were tested for, and found to be absent. Also on testing for malic acid, lead acetate caused a precipitate, which A. H. Allen in "Allen's Food Analysis" says is often the result when dextrin is present. So from the three tests it was thought that sugar in the form of dextrose was present.

Alcohol.—The above work on sugars would also serve to show the amount of alcohol available from such fruit, computed from the glucose reaction. In this fruit the alcohol obtainable would amount to 21.7 per cent of the weight of the fruit, i.e., this rose fruit would yield a comparatively high percentage of alcohol, but which could be obtained only with difficulty on account of the labour involved in gathering.

Acids.—Tests were made for acetic, tannic, gallic, tartaric, oxalic, malic, and citric acids. Only one acid was found, that one being citric, of which there was a very heavy precipitate obtained, not only from the purified sugar solution but also from the original alcoholic solution in which the sugars were originally extracted. When the purified sugar solution was tasted it not only tasted like corn syrup, but very little effect of an acid was noticed by the aid of the tissues of the mouth. Only a slight acid taste remained in the mouth, thus indicating that the amount of acid was very small, and a citrate would be as little noticed in this way as any acid one would expect to find in this or any similar fruit.

Oils.—The berries used in the alcohol extraction were dried as described, weighed, and then ground to a very fine powder. The powder was weighed and weighed the same as the berries, 115 grms. This was then placed in a 500 cc. flask nearly full of ether, and boiled on a water-bath under an inverted condenser. At intervals the ether was removed, care being taken to preserve all the powder,

and fresh ether substituted. After 279 hours of extracting the oil obtained was cleared of ether, alcohol, and water by distillation, and put into a 125 cc. flask. After being brought to constant weight at 90 degrees of heat centigrade, then bone-black was added with alcohol and after a few hours boiling the extract was filtered off, the ether removed by distillation, and the oil again weighed. There was 1.0485 grms. of oil. This was saponified by adding 25 cc. normal NaOH and 25 cc. of 95 per cent alcohol, and boiling under a return condenser for twenty-six hours. An attempt was made to separate the hydrocarbons and waxes by the ether method, but this seemed impossible on account of having first used a water solution of NaOH. The alcohol and ether being driven off, the solution was titrated with normal H_2SO_4 , using litmus solution as an indicator. Neutrality was reached after adding 23.27 cc. H_2SO_4 . The saponification equivalent thus given was 606, which placed the oil, or oils, among the palmitates and close to one of the higher paraffins. After strongly acidifying with H_2SO_4 , the fatty acids were distilled over and the first 50 cc. titrated with normal NaOH. The result compared with Reichert's table again placed the oil among the palmitates, and this was taken as conclusive. It should be mentioned that when the first ether extraction of oils was distilled, the liquid left in the distilling flask seemed to contain two oils, one was a dark red wax, the other yellow and of a semi-granular nature. Since the taste of the oil was that of paraffin (this was unmistakable as the taste was identified several times by different parties), and the saponification equivalent placed the oil so near the higher paraffins, there must have been a small amount of one of the waxes present. However, since the work was done with so small amount of oil, the results were satisfactory without determining the fact conclusively. After the first extraction of 279 hours which yielded the above stated amount of oil, the extraction was continued for 275 hours with no change of ether. The remaining oil yielded was determined by weight and added to the first amount. The total oil thus determined was 1.0569 grms. At this rate it would take nearly five bushels of dry fruit to yield two gills of the oil. The odour of the oil, it should be remarked, resembled that of the higher grades of lubricating oils. This fruit contained less oil than any other fruit examined in this laboratory, having only 0.52 per cent as against 6.47 per cent, a very large amount, found in *Viburnum nudum* (R. H. Lott, *CHEMICAL NEWS*, xcix., 169).

Residue from Ether Extract.—The powder from the ether extract was allowed to dry in the air. The remains were very fine, if anything finer than the powder as it had been first placed in the flask. Some of the seeds still remained, rather some pieces of seeds. These were very hard, but on chewing between the teeth they gave no taste or odour. There seemed to be no odour to the residue in general, but when taken into the mouth there was an aroma of used or old coffee grounds. This could not be detected when the nasal passages were kept closed, so must have been an odour and not a taste. Some of this residue was ashed, 3.1684 grms. being taken. The ash yielded was 0.179, thus giving 5.61 per cent of ash from the residue, showing an increase in percentage of ash when compared with the percentage obtained from ashing the original berries. This may or may not be a point which should receive further investigation; nevertheless, it is contrary to the result obtained in the *Viburnum nudum* to which reference has already been made.

In the work upon this fruit my thanks are due to Dr. Nicholas Knight for much aid and many timely suggestions. Cornell College, May 18, 1909.

New Alkaloid obtained from the Bark of Pseudo-cinchona africana.—Ernest Fourneau. From the bark of *Pseudocinchona africana* a new alkaloid of formula $\text{C}_{21}\text{H}_{26}\text{N}_2\text{O}_3$ can be isolated. It is crystalline, insoluble in ether, levorotatory, gives well defined salts, and contains a second alkaloid, soluble in ether, which the author has not yet obtained in the crystalline state.—*C. R.*, cxlviii.

NOTICES OF BOOKS.

Traité Complet d'Analyse Chimique Appliquée aux Essais Industriels. ("Complete Treatise on Technical Analytical Chemistry"). By J. POST and B. NEUMANN. Second French Edition. Translated from the Third German Edition by Dr. L. GAUTIER. Vol. I., Part III. Paris: A. Hermann et Fils. 1909.

THE part of the first volume of the French translation of this standard work contains full details of the analysis of iron by A. Ledebur, and of metals other than iron by Dr. B. Neumann. The second French edition has been thoroughly revised and brought down to the latest possible date, and many important additions have been made—in fact, no trouble has been spared to make the book the most comprehensive practical treatise on technical analysis yet published.

Das Arbeiten mit Farbenempfindlichen Platten. ("The Use of Colour-sensitive Plates"). By Dr. ERNST KÖNIG. Berlin: Gustav Schmidt. 1909.

THIS short monograph gives a popular exposition of the theory and use of orthochromatic plates, which will be of interest both to the amateur and to the practical photographer. Full directions are given for the preparation of plates which are sensitive to colour, and of light filters of various kinds, and practical details relating to the use of colour-sensitive plates, the illumination of the dark room, &c., are also to be found in the book. The illustrations which show the effects of using the plates and light filters in photographing different objects are very striking, and the comments on them will give the reader, particularly the amateur, much assistance in choosing the most favourable conditions for obtaining a successful photograph.

MISCELLANEOUS.

British Association for the Advancement of Science.

—The following were the Officers and Committee of Section B (Chemistry) at the Winnipeg Meeting of the British Association:—

President—Prof. H. E. ARMSTRONG, Ph.D., LL.D., F.R.S.

Vice-Presidents—Prof. F. S. KIPPING, D.Sc., Ph.D., F.R.S.; Prof. W. P. WYNNE, D.Sc., F.R.S.

Secretaries—E. F. ARMSTRONG, D.Sc., Ph.D. (Recorder); T. M. LOWRY, D.Sc.; F. M. PERKIN, Ph.D.; J. W. SHIPLEY, B.A.

The Papers brought before the Section were as follows:—

Prof. H. E. ARMSTRONG—Presidential Address.

Prof. W. A. NOYES—Molecular Re-arrangement in the Camphor Series.

Prof. W. A. BONE—Combustion.

E. H. ARCHIBALD—Atomic Weight of Iridium; Analysis of Potassium Chloroiridate.

E. H. ARCHIBALD and W. A. PATRICK—Electrical Conductivity of Solutions of Iodine and of Platinum Tetraiodide in Ethyl Alcohol.

Dr. A. SPRINGER—Antiputrescent Effects of Copper.

Reports of Committees—

Isomorphous Sulphonic Derivatives of Benzene.

Electro-analysis.

Hydroaromatic Substances.

Aromatic Nitroamines.

Wave-length Tables.

(Joint Meeting with Section A).

Dr. T. M. LOWRY—Report of the Committee on Dynamic Isomerism: Chemical Change in Relation to Luminous Phenomena.

Prof. E. GOLDSTEIN—Three-fold Spectra of Solid Organic Compounds.

E. F. BURTON—Action of Electrolytes in Colloidal Solutions.

Dr. O. HAHN—Methods of Separation of Radio-active Products.

V. E. POUND—Some Phenomena Associated with Radiations from Polonium.

Dr. O. REICHENHEIM—Anode Rays and their Spectra.

Dr. H. S. BRONSON and Mr. A. N. SHAW—Clark and Weston Standard Cells.

Dr. C. J. FOX—Mercurous Sulphate for Standard Cells.

Dr. C. J. FOX—Constancy of the Hydrogen Gas Electrode.

Dr. T. M. LOWRY—Measurement of Rotary Dispersion.

Dr. T. M. LOWRY—New Method of Producing a Cadmium Arc.

G. A. BLISS—New Proof of Weiersthar's Theorem.

Dr. T. M. LOWRY—Mercury and Cadmium Lines as Standards in Refractometry.

Prof. E. RUTHERFORD—Action of α -Rays upon Glass.

T. KONISHITA—Photographic Action of α -Rays.

Prof. H. E. ARMSTRONG—Precipitation of Salts by Non-Electrolytes.

W. BATES—The Action of Light on the Insulating Property of Sulphur.

(Joint Meeting with Section K).

Dr. E. F. ARMSTRONG—Recent Work on the Strength of Wheat.

A. D. HALL and E. J. RUSSELL—Factors Determining the Yield of Wheat.

Prof. R. HARCOURT—Milling Properties of certain Canadian Wheats.

Prof. L. S. KLINK—Individuality in Plants.

Dr. C. SAUNDERS—Wheat Breeding Experiments in Canada.

F. T. SHUTT—Influence of Environment on the Composition of Wheat.

Dr. STOPF—History of the Wheats.

Prof. C. A. ZAVITZ—Influence of Good Seed on Wheat Production.

(Joint Meeting with Section I).

Discussion on "Food"—Prof. H. E. ARMSTRONG and others.

Dr. E. FRANKLAND ARMSTRONG—Proteins: the Relation between Composition and Food Value.

Dr. W. B. HARDY—Strength in Wheat.

Reports of Committees.

Diseased Potatoes.—The Board of Agriculture and Fisheries desire to remind all growers of potatoes that it is their duty under the Destructive Insects and Pests Order of 1908 to report all outbreaks of Warty Disease or Black Scab (*Chrysaphlyctis endobiotica*) on their premises to the Board. The penalty for failing to report the disease is £10. Certain British colonies now require a certificate from the Board with every consignment of potatoes exported to them from this country, to the effect that the potatoes have been grown in a district not infected with this disease. Exporters who require further information can obtain it on application at the offices of the Board.

International Congress of Mining, Metallurgy, Applied Mechanics, and Practical Geology, Düsseldorf, 1910.—In accordance with the resolutions of the last International Congress of Mining, &c., held at Liège in 1905, it has been arranged that the next Congress shall meet at Düsseldorf during the last week of June, 1910, under the auspices of the Rhenish-Westphalian Mining Industry. An influential Committee of Organisation has been formed which is charged with the making of the arrangements for the reading and discussion of papers, visits to places of technical interest, and social entertainments. Further information can be obtained in due course on application to the Secretary of the Iron and Steel Institute (G. C. LLOYD, 28, Victoria Street, London, S.W.), or to the Committee of Organisation, Jacobstrasse, 3-5, Düsseldorf.

THE CHEMICAL NEWS.

VOL C., No. 2599.

(STUDENTS' NUMBER).

UNIVERSITIES AND COLLEGES.

UNIVERSITY OF LONDON.

CANDIDATES for any Degree in this University must either have passed the Matriculation Examination in this University, or be admitted under the Statute which provides that the Senate may admit graduates of or persons who have passed the examinations required for a degree in other Universities approved by it. This and all other Examinations of the University, together with the Prizes, Exhibitions, Scholarships, &c., are open to Women upon exactly the same conditions as to Men.

There are three Examinations for Matriculation in each year; commencing on the second Monday in September, January, and June (or July, as may hereafter be determined).

Every candidate entering for the Matriculation Examination must pay a Fee of £2. If a candidate withdraws his name, or fails to present himself at the Examination, or fails to pass it, the Fee shall not be returned to him.

A Pass Certificate, signed by the Principal, will be delivered to each successful candidate after the Report of the Examiners has been approved by the Senate.

Intending Students (Internal and External) should obtain the "Regulations and Courses" from the Registrar, University of London, South Kensington, S.W.

Several valuable Scholarships and Exhibitions are available to students.

INTERMEDIATE EXAMINATION IN SCIENCE.

The Intermediate Examination in Science will commence on the second Monday in July.

No candidate is admitted to this Examination unless he has passed, or been admitted under the Statute referred to above as exempt from, a Matriculation Examination not later than that of the preceding January.

The Fee for this Examination is £5.

Examination for Honours.

Candidates for Honours in Chemistry will be examined in Inorganic Chemistry, treated more fully than in the Pass Examination. This Examination will consist of two printed papers and a practical examination.

In the Examination for Honours, the Candidate, not being more than 22 years of age at the commencement of the Pass Examination, who most distinguishes himself will receive an Exhibition of £40 per annum for the next two years.

B.Sc. EXAMINATION.

The B.Sc. Examination will be held on the fourth Monday in October.

Candidates for this Examination are required to have passed the Intermediate Examination in Science at least one academical year previously, and to have passed the Matriculation Examination at least three years previously.

The Fee for this Examination is £5.

Examination for Honours.

For the examination for Honours in Chemistry candidates are required to show a general acquaintance with General Theoretical Chemistry, Chemistry of Carbon Compounds, Physical Chemistry, and History of Chemistry since the time of Boyle.

The candidate, being not more than 23 years of age, who most distinguishes himself in Chemistry, will receive £50 per annum for the next two years, with the style of University Scholar.

DOCTOR OF SCIENCE.

The examination for the Degree of Doctor of Science takes place annually within the first twenty-one days of June.

No candidate is admitted to the examination for the Degree of D.Sc. until after the expiration of two Aca-

demical Years from the time of his obtaining the Degree of B.Sc. in this University.

PRELIMINARY SCIENTIFIC (M.B.) EXAMINATION.

This Examination takes place twice in each year,—once, for Pass and Honours, commencing on the second Monday in July; and once for Pass Candidates only, commencing on the third Monday in January.

The Fee for this examination is Five Pounds.

UNIVERSITY OF OXFORD.

Waynflete Professor of Chemistry—W. Odling, F.R.S.
Lees Reader in Chemistry—H. Brereton Baker, M.A., D.Sc., F.R.S.

Every Student must reside in one or other of the Colleges or Halls, or in licensed lodgings, for a period of three years. Students of Chemistry can obtain the degree of B.A. by passing preliminary examinations in Arts and in Science, and a final Honour examination in Chemistry. Chemistry may also be taken as part of the examination for a Pass degree. Graduates of other Universities and other persons suitably qualified can obtain the degree of Bachelor of Science after an approved course of study or research and two years' residence.

University Laboratory.—Demonstrators, W. W. Fisher, M.A., J. Watts, M.A., and J. E. Marsh, M.A., F.R.S., N. V. Sdgwick, M.A., A. F. Walden, M.A., B. Lambert, M.A.—The fee for students working in the Laboratory for three days in the week during the Term is £3; for students working every day, £5.

There are also laboratories which specialise in different parts of the subject:—*Physical Chemistry*, Balliol and Trinity College Laboratory: D. H. Nagel, M.A., H. B. Hartley, M.A., N. Garrod Thomas, B.A. *Inorganic Chemistry*, Christ Church Laboratory: Dr. Baker, W. Akers, B.A. *Quantitative Analysis*, Magdalen College Laboratory: J. J. Manley, M.A. *Jesus College Laboratory*: D. L. Chapman, M.A. *Queen's College Laboratory*: Rev. H. B. Cronshaw, M.A.

Scholarships of about the value of £80 are obtainable at the majority of the colleges, by competitive examination in Natural Science.

More detailed information may be obtained from the Examination Statutes; the Student's Handbook to the University; and from the professors and college tutors.

UNIVERSITY OF CAMBRIDGE.

Professor of Chemistry—William J. Pope, M.A., F.R.S.
Jacksonian Professor of Natural and Experimental Philosophy—Sir James Dewar, M.A., F.R.S.

The Student must enter at one of the Colleges or Hostels, or as a Non-collegiate Student, and keep terms for three years by residence in the University. He must pass the previous examination in Classics and Mathematics, which may be done in any term of residence or before commencing residence. He may then proceed to take a Degree in Arts, either continuing mathematical and classical study, and passing the ordinary examinations for B.A., or going out in one of the Honour Triposes.

A graduate of another University may be admitted as an "advanced" student, and obtain a degree after two years' residence in the University.

The scholarships, ranging in value from £20 to £100 a year, are chiefly given for mathematical and classical proficiency. Scholarships, or Exhibitions, are given for Natural Science at the several Colleges; the dates of the examinations vary, but are always fully advertised.

The Chemical Laboratory of the University is open daily for the use of the Students. The Demonstrators attend daily to give instruction. A list of the lectures is published annually, in June, in a special number of the *Cambridge University Reporter*, which may be had from the Cambridge Warehouse, in Paternoster Row, or through any bookseller.

Non-collegiate Students are allowed to attend certain of the College Lectures and all the Professors' Lectures,

and have the same University status and privileges as the other Students. Full particulars may be obtained by forwarding a stamped directed envelope to the Assistant Registrar, Cambridge, from the *Cambridge University Calendar*, or from the "Students' Handbook to Cambridge."

UNIVERSITY OF DUBLIN.

TRINITY COLLEGE.

Professor of Chemistry—Sydney Young, D.Sc., F.R.S.
Professor of Applied Chemistry—Emil A. Werner, F.C.S., F.I.C.

Demonstrator—W. C. Ramsden, F.C.S.

Junior Demonstrators—W. R. G. Atkins, B.A., T. A. Wallace.

The general Quantitative and Research Laboratories include working accommodation for about 130 Students. The Laboratories will open on October 1st. Lectures will commence about November 1st.

The Laboratories and the Lectures of the Professor of Chemistry can be attended by Students who do not desire to reside in the University or proceed to its Degrees.

The full Course of General and Analytical Chemistry occupies three years, but a Student is free in his third year to devote most of his time to a special department of Pure or Technical Chemistry. Students can enter for any portion of the Course. The Lectures delivered are:—

1. *Inorganic Chemistry and Chemical Philosophy*.—Elementary, first year; Advanced Inorganic Chemistry, second year; Physical Chemistry, third year.
2. *Organic Chemistry*.—General, second year; advanced, third year.
3. *Metallurgy*.—A Course for Engineering and Technical Students.
4. *Agricultural Chemistry*.—Theoretical and Practical Courses.

The Laboratories are open every day from 10 to 5 o'clock (except Saturdays, when they close at 1 o'clock).

The *Summer Course of Practical Chemistry for Medical Students* begins early in April and terminates about the end of June.

A special course for Dental Students will be given.

The University of Dublin grants the Degree of Doctor of Science to graduates of Master's standing whose independent researches in any branch of Science are of sufficient merit.

By recent decrees, Prizes in Chemistry and Physics will be given in future at the October (Arts) Entrance Examination, and also at the Terminal Examinations of the Junior and Senior Freshmen Years.

Similarly, two Science Scholarships will be obtainable by Undergraduates, and tenable for five years. The Foundation Scholars receive £20 per annum, they have free commons, and their chambers for half the charge paid by other students; their tutorial fees are at one-fourth the usual rates.

KING'S COLLEGE.

Senior Professor of Chemistry—J. M. Thomson, LL.D. F.R.S.

Professors—Herbert Jackson, F.C.S., and P. H. Kirkaldy, F.C.S.

Lecturer and Demonstrators—H. L. Smith, B.Sc., S. W. Collins, B.Sc., and L. Hinkel.

The Academic Year consists of Three terms. The days fixed for the commencement of Terms in 1909-1910 are Oct. 6, Jan. 12, and April 20.

Students of the First Year are admitted to the Course of Theoretical and Applied Chemistry. The Course commences with a view of the conditions suitable for the production of Chemical Phenomena, after which the laws of Chemical Attraction are discussed, and the Non-metallic Elements and their principal compounds are described. The Metals and their principal compounds are next examined, care being taken to point out the applications of the Science to the Arts; and the processes of the different Manufactures and of Domestic Economy are explained and illustrated. Examinations of

the Class, both *viva voce* and by written papers, are held at intervals during the course at the usual Lecture hour.

Second Year.—Students attend in the Laboratory twice a week, and they go through a course of Chemical Analysis, both by liquid tests and the blowpipe, analysis of ores, liquids, &c., and Elementary Volumetric Analysis.

Experimental and Analytical Chemistry in the Laboratory.—The object of this Class is to afford to Students who are desirous of acquiring a knowledge of analysis, or of prosecuting original research, an opportunity of doing so under the superintendence of the Professor and Demonstrator; Students may enter, upon payment of extra fees, at any time except during the vacation, and for a period of one, three, six, or nine months, as may best suit their convenience. The laboratory hours are from ten till four daily, except Saturday.

In addition to the Laboratory Fee, each Student defrays the expenses of his own experiments. The amount of this expense, which is comparatively trifling, is entirely under his own control.

Fees.—Chemistry: Winter Session, £5 5s.; Summer Session, £3 3s. Practical Chemistry: Winter Session, £8 8s.; Summer Session, £4 4s. Experimental and Analytical Chemistry—Five days a week: One month, £4 4s.; One Term, £10 10s.; Two Terms, £18 18s.; Three Terms, £26 5s. Three days a week: One month, £2 12s. 6d.; One Term, £6 6s.; Two Terms, £11 11s.; Three Terms, £15 15s.

For fuller details the separate Syllabuses provided for each class should be consulted.

METALLURGY.

Professor—A. K. Huntington, A.R.S.M., F.I.C., &c.

The following subjects are treated in the Lectures: The Selection and Economic Preparation of Fuel and of Refractory Materials; the methods by which metals are obtained from their ores, and the means by which they are rendered suitable for the various requirements of the Arts.

Particular attention is paid to the study of the Nature and Properties of Metals and Alloys available for Constructive Purposes.

In the Metallurgical Laboratory, which is always open during College hours, the relation between the Chemical Composition of Metals and their Mechanical Properties may be studied by the aid of Testing Machinery.

Fee, £3 3s. for the Course.

PHOTOGRAPHY.

Lecturer—Prof. J. M. Thomson, LL.D., F.R.S.

For particulars apply to Prof. Thomson.

EVENING CLASSES.

Classes for Evening Instruction in various subjects are held during the Winter Session.

UNIVERSITY COLLEGE.

(UNIVERSITY OF LONDON).

Professors—Sir William Ramsay, K.C.B., LL.D., F.R.S. (Inorganic and Physical Chemistry); J. Norman Collie, Ph.D., F.R.S. (Organic Chemistry)

Assistants—E. C. C. Baly, F.I.C.; S. Sniles, D.Sc.; N. T. M. Wismore, M.Sc.; Katharine A. Burke, B.Sc.; R. W. Gray, Ph.D.; and W. B. Tuck, D.Sc.

The Session is divided into three Terms, as follows:—First Term, from October 4 to December 17; Second Term, from January 11 to March 23; Third Term, from April 17 to July 7.

Introductory Course of Inorganic Chemistry.

Tuesday and Thursday, at 9. Practical, Thursday, 2 to 3.30, or 3.30 to 5. Fee, £10 10s.

This Course treats of the chief physical and chemical characters of the Non-metallic Elements, their preparation and characteristic tests.

Junior Course of Inorganic Chemistry.

First and Second Terms: The Class meets four times a week, on Mondays, Wednesdays, Fridays, and Saturdays, at 9, for Lectures, Examinations, and Exercises.

In this Course the physical principles bearing on Chemistry are first discussed, and the Chemistry of the Elements and their compounds is treated in considerable detail, under the headings—Elements; hydrides, halides, oxides, sulphides, &c., borides, carbides and silicides, nitrides, phosphides, &c., and alloys. Special attention is devoted to substances of commercial importance. The concluding Lectures are devoted to Physical Methods and their bearing on Chemical Problems.

Third Term: Lectures will be given on Mondays and Fridays at 9 and on Wednesdays at 11, on the chief types of Carbon Compounds.

Fees: Course, £7 7s.; First or Second Terms, £4 4s.

A Practical Class will meet throughout the Session.

Course of Physical Chemistry.

October to February: Tuesday and Thursday at 9. February to June: Monday and Saturday at 9.

The Principles of Chemistry will be especially considered, comprising the Atomic Theory, Chemical Classification, the Periodic Law, Thermal Chemistry, Dissociation, the Application of Physical Methods to the Solution of Chemical Problems, and the influence of Mass and Temperature on the progress of Reactions. Special attention is paid to the most recent Chemical Theory researches.

Fees:—Courses, £5 5s.; Term, £2 2s.; for a second course, £1 1s.

Senior Course of Inorganic Chemistry.

This Course will begin about the middle of February; Tuesday and Thursday at 9. Fee, £3 3s.

Electrochemistry.

October to February: Monday and Saturday at 9. February to June: Tuesday and Thursday at 11. Fee for the Course, £5 5s.

Organic Chemistry.

Mon. at 12, Wed. and Fri. at 9, during the session.

This Course is suitable for Students who intend to study Chemistry from a scientific standpoint. No previous knowledge of Organic Chemistry is expected of those attending the Class, which should, however, be taken concurrently with the Course of Physical Chemistry, and with Practical Organic Chemistry in the Laboratory.

Fee:—For the Course, £6 6s.; for a Term, £2 12s. 6d.; for a Second Course, £3 3s.

An Advanced Course will be held twice a week throughout the Session for those engaged in prosecuting research in Organic Chemistry. Fee, £5 5s.; Term, £2 2s.

Practical Classes.

Practical Classes in Inorganic and Organic Chemistry are conducted by the Assistants.

Laboratories of General and of Organic Chemistry.

The Laboratories are open daily from 9 a.m. to 5 p.m., Saturdays excepted, from October until the middle of July, with a short recess at Christmas and at Easter.

Fees: for the Session, £26 5s.; six months, £18 18s.; three months, £10 10s.; one month, £4 4s.

Three specified days a week:—for the Session, £15 15s.; six months, £11 11s.; three months, £6 6s.; one month, £2 12s. 6d., exclusive of expense of materials. Students may enter at any period of the Session.

When accompanied by, or preceded by, attendance on the Lectures on Inorganic and Organic Chemistry, the Laboratory Courses qualify Students in the application of Chemistry to Manufactures, Metallurgy, Medicine, or Agriculture, &c.

There is also a Chemical Library containing the chief Journals and Standard Works on Chemistry.

Certificates of Honour are granted to competent Students on the work done during the Session. Several valuable Scholarships are available to students.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY.

Emeritus Professor—W. A. Tilden, D.Sc., F.R.S.

Professor and Director of the Chemical Laboratories—Sir T. E. Thorpe, C.B., F.R.S., &c.

Assistant Professors—M. O. Foster, Ph.D., D.Sc., F.R.S.; G. T. Morgan, D.Sc., A.R.C.S.; J. C. Phipps, M.A., Ph.D., B.Sc.

The Imperial College of Science and Technology, incorporated under the Royal Charter of July 8, 1907, is an institution or group of associated colleges with its principal seat at South Kensington.

The purposes of the Imperial College are to give the highest specialised instruction, and to provide the fullest equipment for the most advanced training and research in various branches of science, especially in its application to industry; and to do all and any of such things as the Governing Body consider conducive or incidental thereto, having regard to the provision for those purposes which already exists elsewhere.

For these purposes, the Governing Body, subject to the provisions of the Charter, are to carry on the work of the Royal College of Science, and the Royal School of Mines, and may establish Colleges and other Institutions or Departments of Instruction. Any Institution or Department so established, and, subject to the conditions of the Charter, the Central Technical College of the City and Guilds of London Institute, are to be integral parts of the Imperial College; and the Central Technical College is to be called and known in future as the City and Guilds College.

Subject to agreement with the authorities of any College or other Institution, the Governing Body may by resolution recognise that College or Institution or any Department thereof, as being in association with the Imperial College for all or any of the purposes of the Charter, but no such resolution is to be valid or operative until allowed by the King in Council.

The Charter further provides that the Imperial College shall be established in the first instance as a School of the University of London. Students of the Imperial College who have matriculated at the University of London may therefore proceed to the Science degree of the University as "Internal Students."

Attention is particularly directed to the conditions of admission and to the extended facilities for Research Work.

The ordinary courses of instruction are planned so as to extend over four years, and are generally similar for all divisions during the first year, and to a less extent during the second year, after which they are specialised according to the particular course which the student is taking.

The following Diplomas have been awarded in the past to Students of the several constituent Colleges:—

The Associateship of the Royal College of Science (A.R.C.S.) in one or more of the following divisions:—Mechanics, Physics, Chemistry, Botany, Zoology, Geology.

The Associateship of the Royal School of Mines (A.R.S.M.) in one or more of the following divisions:—Metallurgy, Mining.

The Associateship of the City and Guilds Institute (A.C.G.I.) in one or more of the following divisions:—Chemistry, Engineering (Civil and Mechanical), Engineering (Electrical).

The instruction in Chemical Science embraces:—

1. Courses of lectures on the laws and general principles of Chemistry, including the special study of compounds of carbon, usually called "Organic Chemistry"; on the theory and methods of Chemical Analysis; and on Physical Chemistry.

2. A systematic Laboratory course for the practice of Qualitative and Quantitative Analysis.

An examination will be held at the end of each course of instruction, and all candidates for a Diploma in Chemistry will be required to qualify in each successive stage.

A Laboratory course is provided for advanced students desirous of acquiring a knowledge of the methods employed in research and for the prosecution of Chemical Investigations.

Full details can be obtained from the College Calendar, published by Eyre and Spottiswoode (or through any bookseller), price 6d.

THE SCHOOL OF PHARMACY OF THE PHARMACEUTICAL SOCIETY OF GREAT BRITAIN.

The 67th Session will commence on Sept. 29, 1909.

Professors—Chemistry, Arthur W. Crossley, D.Sc., Ph.D., F.I.C., F.R.S.; Pharmaceutics, Henry G. Greenish, F.I.C., F.L.S. (Dean).

A Course of Lectures on Physical, Inorganic, and Elementary Organic Chemistry commences in October and terminates at the end of June. An Advanced Course of Lectures begins in October and extends to the end of March. These Lectures are adapted to the requirements of Pharmaceutical and Medical Students, and also of those who are proceeding to degrees at the University of London, or who are preparing for the examinations of the Institute of Chemistry.

Entries may be made for single classes. Certificates of attendance at the two Courses of Lectures on Chemistry and at the Chemical Laboratories are accepted as evidence of chemical training by the Institute of Chemistry in connection with the Examinations for the Associateship, and also by the Conjoint Board of the Royal Colleges of Physicians and Surgeons, as well as by other examining bodies. Certificates of attendance at the Course of Pharmacy is also accepted by the Conjoint Board.

Prospectuses and further information may be obtained from the Dean of the School, 17, Bloomsbury Square, London, W.C.

UNIVERSITY COLLEGE OF WALES, ABERYSTWYTH. UNIVERSITY OF WALES.

Director of the Edward Davies Chemical Laboratories and Professor—J. J. Sudborough, D.Sc. (Lond.), Ph.D. (Heidelberg), F.I.C.

Assistant Lecturers and Demonstrators—A. Brooke, Ph.D. (Strass.), and T. C. James, M.A. (Cantab.), B.Sc.

Lecturer in Agricultural Chemistry—J. Jones Griffith, B.Sc. (Wales).

The College is open to men and women students above the age of sixteen years. The Session commences on Oct. 5th, on which day all Students will be expected to meet the Professors in the Examination Hall of the College.

Lecture Courses.—(1) Intermediate Science Course; four lectures weekly throughout the Session. (2 and 3) B.Sc. Courses; A, three lectures weekly on Organic Chemistry; B, three lectures weekly on General and Physical Chemistry. (Courses A and B will generally be given in alternate Sessions; for 1909-1910, Course A). (4 and 5) Courses in Agricultural Chemistry. For students in their first year, 3 lectures, and for those in their 2nd year, 2 lectures weekly during the Michaelmas and Lent terms.

Laboratory Courses.—The Laboratories are open daily from 9 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays. Regular Courses of practical work, suitable for the B.Sc. degree of the Universities of London and Wales, or for the Associateship of the Institute of Chemistry, can be followed. Facilities are given for Students wishing to undertake research work. Special Courses will be arranged for those who intend to follow Medicine or Pharmacy, or any one particular branch of Applied Chemistry, always provided that such Students possess the requisite knowledge of Theoretical Chemistry. The hours will be arranged, as far as possible, to suit the requirements of the individual Student.

The College is recognised by the University of Edinburgh and the Royal University of Ireland, and by the Colleges of Physicians and Surgeons of England, Scotland, and Ireland as an institution at which the instruction necessary for their respective Diplomas in Medicine, in Chemistry, Physics, and Biology may be given. One year for graduation in Medicine and two years for graduation in Science may be spent at Aberystwyth.

Fees.—The Fee for the whole Session, if paid in advance, is £10; if paid by Single Terms, for the first term of attendance in each Session, £4; for the second term,

£3 10s.; for the third term, £3. These composition fees enable the Student to attend any or all the Classes of the College, with the exception that a small extra fee is charged for Laboratory Instruction. Thus, for Practical Chemistry, the additional fee is, for six hours' work per week, 12s. 6d. per term, and for twelve hours, 25s. per term. The fees for those who desire to spend several days weekly in the laboratory may be learned on application to the Registrar. Fee for a single Lecture Course £1 per term.

Scholarships and Exhibitions varying in value from £10 to £40 per annum will be offered for competition at examinations which commence on September 21, and exhibitions are awarded at the end of the Session on the results of the class examinations.

Intending Students requiring further information are recommended to write to the Registrar for a copy either of the General Prospectus or of one of the Special Prospectuses issued for the Agricultural and Normal Departments.

UNIVERSITY COLLEGE OF NORTH WALES, BANGOR.

A CONSTITUENT COLLEGE OF THE UNIVERSITY OF WALES.

Chemistry.—Professor, K. J. P. Orton, M.A., Ph.D., F.I.C. Assistant Lecturer and Demonstrator, Alice E. Smith, B.Sc. Assistant Lecturer in Agricultural Chemistry, R. Gaunt, Ph.D., M.Sc. Junior Demonstrator, J. O. Hughes, B.Sc.

Physics.—Professor, E. Taylor Jones, D.Sc. Assistant Lecturers and Demonstrators, A. H. Ferguson, B.Sc., and W. E. Williams, B.Sc.

The Session opens October 5th, 1909. All regular classes are open to men and women students above the age of 16 years. The following Courses of Lectures will be given.

Intermediate Course.—Inorganic Chemistry and Elementary Physical Chemistry. Fee for the Session, £3 13s. 6d.

B.Sc. Course.—Organic Chemistry. Fee for the Session, £3 3s. Advanced Lectures on Organic Chemistry, £1 1s. *Agricultural Chemistry*.—Fee, £2 2s.

Laboratory Courses.—The laboratory is open on five days of the week from 10 a.m. to 5 p.m. for instruction in Chemical operations and in the Application of Chemistry to Medicine and the Industrial Arts. Fees: six hours per week, £1 1s. per Term; twelve hours, £2 2s.; eighteen hours, £3 3s. Composition Fee for all Laboratory Classes of the Intermediate Science Course taken in one year, £4 4s.

The Chemistry, Botany, Zoology, and Physics Courses are recognised for Medical graduation in the Universities of Edinburgh and Glasgow, and by the Conjoint Boards of the Royal Colleges of Surgeons and Physicians, and students can make one *Annus medicus* at the college. Students are prepared for the First Examination of the Universities mentioned, the First Examination for Medical Degrees of the University of London, and of Conjoint Board of the Royal Colleges of Surgeons and Physicians. The Science Courses are recognised for part of the science degree course of the University of Edinburgh.

UNIVERSITY COLLEGE OF SOUTH WALES AND MONMOUTHSHIRE, CARDIFF.

Professor—C. M. Thompson, M.A., D.Sc., F.C.S.

Assistant Professor—E. P. Perman, D.Sc., F.C.S.

Demonstrator—R. D. Abell, D.Sc., Ph.D., F.I.C., F.C.S.

Lecturer in Metallurgy—A. A. Read, F.I.C., F.C.S.

The Session commences October 5th, and terminates on June 24th, and is divided into three terms.

The Junior Course (delivered during the Michaelmas term only) consists of about 30 lectures, and will cover the subjects prescribed for the Matriculation examinations of the University of Wales and the University of London. Fee, £2 2s.

The Intermediate Course consists of about 80 lectures held during the Lent and Summer terms in continua

tion of the Junior Course; together with laboratory practice it forms the qualifying course for the Intermediate Examination of the University of Wales, and will cover the subjects required for the Intermediate Examination in Science (Part I.) of the University of London. Fee, £4 4s.

The Senior Course consists of about 50 lectures on Organic Chemistry; Fee, £3 3s.

The following lectures on Metallurgy will be given by Mr. Read:—10 lectures on Fuel; Fee, 10s. 6d. 20 lectures on General Metallurgy; Fee, £1 1s. 30 lectures on the Manufacture of Iron and Steel; Fee, £1 1s. A practical course on Iron and Steel Analysis will also be held, and practical instruction in Dry Assaying will be given in the Metallurgical Laboratory, which is fitted with the necessary furnaces and apparatus.

In the laboratory each student works independently, so that the course of study may be adapted to the requirements of the individual. Hours, 9 to 1 and 2 to 5; Saturday, 9 to 1. Fees—Six hours per week, £2 2s. per term; twelve hours, £3 3s. per term; eighteen or more hours, £4 4s. per term.

Registered medical students can prepare for the Intermediate M.B. Examination of the University of London, and spend three out of their five years of medical study in Cardiff. Medical students wishing to graduate at a Scottish University, or preparing for a Conjoint Board Surgical and Medical Diploma, or for the Diploma of the Society of Apothecaries, can spend two years in Cardiff. For further information see the prospectus of the Faculty of Medicine, which may be obtained from the Registrar.

The College is recognised as an institution at which two years of the course for the degree of Bachelor of Science of the University of Edinburgh may be spent.

Students by making a payment of £10 at the commencement of each session may compound for all lecture fees for the whole session. Laboratory fees are not included in the composition fee, but Students preparing for the Science Examinations of the University of Wales and of the University of London may, by making a payment of £13 13s. at the commencement of each Session, compound for both Lecture and Laboratory Fees during the Session.

At the entrance examination in September, and the annual examination in June, several scholarships and exhibitions are awarded. Great importance is attached to special excellence in one subject.

The College Prospectus, and also further information as to scholarships, may be obtained from the Registrar.

A Hall of Residence for Women Students is attached to the College.

UNIVERSITY OF BRISTOL.

Professor of Chemistry—Francis Francis, D.Sc., Ph.D., F.I.C.

Lecturer (Physical Chemistry)—James W. McBain, M.A., Ph.D.

Lecturers—Oliver C. M. Davis, B.Sc., F.I.C., F. W. Rixon, M.Sc., Ph.D., F.C.S.

Lecturers (Agricultural Chemistry)—Max Nierenstein, Ph.D., C. T. Gimmingham, A.I.C.

Lecture Assistant—J. H. Sturgess.

The session 1909-1910 will begin on October 1. Day and evening lectures and classes are held throughout the Session. In the Chemical Department lectures and classes are given in all branches of theoretical chemistry, and instruction in practical chemistry is given daily in the chemical laboratory. A Laboratory has been fitted with a complete equipment for all ordinary measurements in Physical Chemistry. The department of experimental physics includes various courses of lectures arranged progressively, and practical instruction is given in the physical and electrical laboratories. The Department of Engineering and the Constructive Professions is designed to afford a thorough scientific education to students intending to become engineers, or to enter any of the allied professions,

and to supplement the ordinary professional training by systematic technical teaching. This department includes courses specially arranged for students intending to become civil, mechanical, electrical, mining, or motor car engineers, surveyors, or architects. Those who attend the mechanical engineering course enter engineering works during the six summer months, and, in accordance with this scheme, various manufacturing engineers in the neighbourhood have consented to receive students of the University into their offices and workshops as articled pupils at reduced terms. Medical education is provided by the Faculty of Medicine of the University. Several Scholarships are tenable at the University. Full information may be obtained from the Registrar.

DAY LECTURES.

Inorganic Chemistry.

The Courses treat of the principles of Chemistry, and of the Chemistry of the Non-Metals and Metals.

Introductory Course.—Three Lectures a week will be given during the First and Second Terms, and at least one Lecture a week during the Third Term. Fee, £3 13s. 6d.

General Course.—Three Lectures a week will be given throughout the Session. Fee, £3 13s. 6d.

Systematic Physical Chemistry (a course extending over two Sessions)—Two Lectures a week will be delivered throughout the Session. Fee, £3 13s. 6d.

Electro-chemistry.—One Lecture a week will be given during the Third Term. Fee, £1 1s.

Advanced Course.—Two Lectures a week will be given throughout the Session. Fee, £3 13s. 6d.

Organic Chemistry.

General Course.—Three Lectures a week will be given throughout the Session. Fee, £3 13s. 6d. An advanced course of lectures will also be given one day a week during the session. Fee, £2 2s.

Colloquium.

A weekly Colloquium will be held by members of the Staff to discuss recent advances in the various departments of Chemistry. Students and others interested are invited to attend.

Practical Chemistry.—Laboratory Instruction.

The Chemical and Metallurgical Laboratories will be open daily from 9 a.m. to 5 p.m., except on Saturdays, when they are open to senior students only. Instruction will be given in the Laboratory in all branches of Inorganic, Organic, and Physical Chemistry. Special facilities will be afforded to those who desire to carry out research or to study Practical Chemistry as applied to the different processes employed in the Arts and Manufactures. Fees in Guineas—

Days per Week ..	Five.	Four.	Three.	Two.	One.
Per Session ..	15	12½	10	7½	5
„ Two Terms ..	11	9	7½	5½	3½
„ One Term ..	7	6	4½	3½	2½

Students may arrange to divide their days of laboratory work into half-days. Special facilities are afforded for Research and Post graduate work.

Chemical Scholarship.—Among others, a Chemical and a Metallurgical Scholarship each of £25 are offered for competition.

EVENING LECTURES.

A course of Lectures dealing with the theories of modern Chemistry will be delivered during the First and Second Terms. Fee, 10s. 6d.

Practical Chemistry.—Laboratory Instruction.—The Laboratory will be open one evening a week from 6 till 9. Instruction will be given in Qualitative and Quantitative Analysis, and in the Preparation of Chemical Products. Fees:—Two Terms, 21s.; One Term, 12s. 6d.

The University of Bristol has been approved by the Council of the Institute of Chemistry as a College at which all the subjects required for the admission of Associates to the Institute are taught.

MERCHANT VENTURERS' TECHNICAL COLLEGE, BRISTOL. CHEMISTRY.

Professor—J. Wertheimer, B.Sc., B.A., F.I.C., F.C.S.

Lecturers—H. A. M. Borland, A.R.C.S.; E. E. Elt, B.Sc.

Demonstrators—E. H. T. Parker; D. A. Baker.

Assistants in Chemical Laboratory—W. F. Phillips and C. Cox.

In consequence of the foundation of the University of Bristol, the College now restricts its work to Applied Chemistry in the daytime; Pure Chemistry is taught at the University College. The Engineering work of the University College has, on the other hand, been transferred to this College.

The College Evening Classes commence on Monday, September 27.

Further detailed information may be obtained from the College Calendar, price 6d., or the Prospectus for Day or Evening Classes (free).

UNIVERSITY OF BIRMINGHAM.

Professor—Percy F. Frankland, Ph.D., M.Sc., LL.D., F.R.S., F.I.C.

Assistant Lecturers and Demonstrators—Alex. Findlay, M.A., D.Sc., Ph.D.; Hamilton McCombie, M.A., Ph.D., B.Sc., A.R.C.S., A.I.C.; C. K. Tinkler, D.Sc., and T. J. Murray, Ph.D., M.Sc.

The Session will be opened on October 4th, 1909.

The Chemical Department is now housed in the new University buildings at Bournbrook.

Lecture Courses.

First Year.—A. This part of the course is arranged (1) to give a full exposition of the general principles of Chemical Science, (2) for the systematic study of the properties of the more important elements and their compounds, and (3) to indicate the chief applications of Chemistry in the Arts and Manufactures. Three hours weekly during the Winter and Spring terms. Mondays, Wednesdays, and Thursdays at 9.30 a.m. Fee, £5 5s. B. This part of the course includes an introduction to the study of Organic Chemistry, with a description of the properties, relations, and methods of preparation of the more important groups of Carbon Compounds. Three hours weekly during the Summer term. Mondays, Wednesdays, and Fridays, at 9.30 to 10.30 a.m. Fee, £1 11s. 6d.

Second Year.—*Advanced Organic Chemistry.*—This course extends over two years, and is divided into two parts:—(a) Carbon Compounds of the Fatty Series; (b) Aromatic and other Cyclic Compounds. Only one of these parts will be taken in each year. The class meets twice weekly by arrangement during the Winter and Spring terms. Fee, £2 2s. *General and Physical Chemistry.*—This course will deal in outline with the more recent developments of Theoretical Chemistry. The class meets once weekly by arrangement during the three terms. Fee, £1 11s. 6d.

Third Year.—A further Course in Advanced Organic Chemistry will deal with one of the above parts of the Course. The class meets two hours weekly by arrangement during the Winter and Spring terms. Fee, £2 2s. A further Course on General and Physical Chemistry, in which special subjects attracting attention at the time receive treatment. Fee, £1 11s. 6d.

Fourth Year.—For students preparing for the B.Sc. degree with Honours in Chemistry.

Practical Chemistry.

The instruction in Practical Chemistry extends over four years in the case of the Honours Degree. The Laboratory will be open daily from 9.30 to 5, except Saturdays, when it closes at 1 p.m.

	All day.	Three hours per day.	Three hours per day; five days a week.	Three hours per day; three days a week.
	Guineas.	Guineas.	Guineas.	Guineas.
One Term ..	7	4½	4	2½
Two Terms ..	13	8½	7½	5
Three Terms	18	12	11	6½

A Course of short demonstrations and exercises is given by the Professor or one of his Assistants once a week. All first-year Students are required to attend, unless exempted for special reasons by the Professor. No Fee.

Special facilities are given to Advanced Students for the prosecution of original research.

Metallurgy.

There is a separate University department for Metallurgical students in which provision is made for instruction in assaying, &c.

Scholarships.

Priestley Scholarships.—Three Open Scholarships in Chemistry of the value of about £96 each are awarded annually in June.

Ascough Scholarship.—One Open Scholarship of the value of about £30 is awarded annually in July.

Bowen Scholarship.—One Open Scholarship in Metallurgy, value about £96, is awarded annually in June.

For particulars apply to the Registrar.

Excursions.

During previous Sessions permission has been obtained to visit some of the great factories in or near Birmingham, in which chemical and metallurgical industries are carried on. Students have thus had most valuable opportunities of gaining a practical acquaintance with some branches of Applied Science. The privilege thus courteously granted by several manufacturers will, it is hoped, be enjoyed in every future Session. The excursions will be conducted by the Professor or Lecturers.

CITY OF BRADFORD TECHNICAL COLLEGE.

Principal—Prof. W. M. GARDNER, M.Sc.

DEPARTMENT OF CHEMISTRY AND DYEING.

Professor of Chemistry and Dyeing—W. M. Gardner, M.Sc.

Assistant Professor of Chemistry—B. North, A.R.C.Sc. (Lond.).

Lecturers in Chemistry—L. L. Lloyd, Ph.D.; H. H. Hodgson, M.A., B.Sc., Ph.D.; S. F. Stoll, F.C.S.

Demonstrators in Chemistry—A. E. Findley, B.Sc.; S. M. Sutcliffe, F.C.S.

Lecturer in Physics—J. A. Tomkins, A.R.C.Sc. (Lond.).

Demonstrator in Physics—E. B. Walker.

Lecturer in Dyeing—A. B. Knaggs, F.C.S.

Demonstrator in Dyeing—T. Brooke.

Lecturer in Gas Manufacture—W. Cianfield.

Lecturer in Botany, Biology, and Pharmacy—W. West, F.L.S., Ex. Pres. Yorkshire Naturalists' Union.

The following courses of instruction are provided—

I. *General Chemistry Course*, extending over four years, and including Lectures in Inorganic, Organic, and Technological Chemistry, Principles of Analysis, Technical Analysis, Electro-chemistry, Physical Chemistry, Crystallography, Fuels, Lighting and Ventilation, Physics, Mathematics, Mechanics, with Laboratory work in Chemistry, Physics, Bacteriology, and Microscopy.

II. *Chemistry and Dyeing*, extending over four years. Includes most of the above subjects, along with Lectures and practical work in Dyeing, Colour matching, &c.

III. *Chemical Engineering*. Three years' course, preparing Students for positions in Chemical Works, Sewage Works, &c.

IV. *Sanitary Science*. One year's Course, recognised by the Sanitary Institute as preparing for their certificate examination. Subjects: Chemistry, Physics, Sanitary Engineering, Sanitary Law, Building Construction, Drawing, Physiology, and Bacteriology.

V. *Dyeing*. Special Courses for Graduates in Chemistry, and for Drysalers, Colour Merchants, &c.

VI. *Textile and Dyeing*. Arranged for those Students who desire to study the two subjects simultaneously.

VII. *First Professional Examination, Conjoint Medical Board* (M.R.C.S., L.R.C.P.), London.—Attendance at the College and College Certificates in Chemistry, Physics, and Biology are recognised by the Conjoint Board for Medical Studies as a qualifying curriculum.

VIII. *General Pharmaceutical Course.* Prepares for the Minor and Major Pharmaceutical Examinations. Each extends over two years on four half-days per week, and includes Chemistry and Physics, Botany, Biology, Materia Medica, Pharmacy, and Dispensing.

ROYAL AGRICULTURAL COLLEGE, CIRENCESTER.

CHEMICAL DEPARTMENT.

Professor—Prof. E. Kinch, F.C.S., F.I.C.

Assistant—W. James.

Systematic courses of Lectures are given on the various branches of Chemistry in its relation to Agriculture, illustrated by experiments, and by the collections in the College Museum. They comprise the laws of Chemical Combination and the general Chemistry of mineral bodies, and of the more frequently occurring bodies of organic origin, with the relationships of their leading groups; and, finally, the applications to practical operations of the Chemistry of the atmosphere, of soils and manures, of vegetation, of stock feeding, and of the processes and products of the dairy.

In the Laboratory practical instruction is given in the construction and use of apparatus and in Chemical manipulation and analysis, both qualitative and quantitative. After studying the simple operations and the properties of the commonly occurring substances, the Students are taught to analyse a series of compounds, and apply the knowledge thus obtained to the analysis of manures, soils, waters, feeding stuffs, dairy products, and other substances met with in the ordinary course of Agricultural practice. Chemico-agricultural researches are undertaken by the senior Students under the direction of the Professor and his Assistants.

THE UNIVERSITY OF LEEDS.

Professor of Chemistry—Arthur Smithells, B.Sc., F.R.S.

Professor of Organic Chemistry—Julius B. Cohen, Ph.D., B.Sc.

Lecturer on Physical Chemistry—H. M. Dawson, D.Sc., Ph.D.

Assistant Lecturers and Demonstrators—W. H. Perkins, B.Sc.; W. Lowson, B.Sc., F.I.C.

Demonstrators—H. Calam, M.Sc.; A. T. King, B.Sc.; J. Marshall, B.Sc.

The Session begins October 4, 1909.

Lecture Courses.

1. General Course of Chemistry.—Monday, Wednesday, and Friday, at 11.30 a.m. Fee for the Course, £4 4s.

2. Advanced Inorganic Chemistry.—Metals. Monday, Wednesday, and Friday, at 9.30 a.m. Fee, £3 13s. 6d.

3. Advanced Inorganic Chemistry.—Non-metals. Tuesday, Thursday, and Saturday, at 9.30 a.m. Fee, £3 13s. 6d.

4. Organic Chemistry.—Tuesday, Thursday, and Saturday at 12 noon. Fee £3 13s. 6d.

5. Honours Courses—(a) Organic Chemistry: Monday, Wednesday, and Friday at 12 noon in the First and Second Terms; fee, £2 12s. 6d. (b) History of Chemistry: Monday, Wednesday, and Friday at 9.30 a.m. in the First Term; fee, £1 11s. 6d. (c) Physical Chemistry: Monday, Wednesday, and Friday at 9.30 a.m. in the Second and Third Terms; fee, £2 12s. 6d. (d) Electro-chemistry: One hour weekly; 3s. 6d.

6. Chemistry of Food and Drugs—Special class for Students taking Final Examination of the Institute of Chemistry in Branch E (Food and Drugs). £2 2s.

Laboratory Courses.

The University Laboratory will be open daily from 9 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it will close at 1 p.m.

Fees for the Session—Students working six days per week, £21; five, £18 18s.; four, £16 16s.; three, £13 13s.

Practical Course in Sanitary Chemistry.—Tuesdays and Thursdays from 2 to 5 from April to June. Fee, £5 5s.

Tinctorial Chemistry and Dyeing Department.

Professor—Arthur G. Green, M.Sc., F.I.C.

Lecturer and Research Chemist—A. G. Perkin, F.R.S., F.I.C.

Assistant Lecturer—Ian Q. Orchardson, B.Sc.

Demonstrator—G. H. Frank, B.Sc.

The Courses extend over periods of three or four years, and are intended for those who wish to obtain a full scientific and practical education in the art of dyeing, colour manufacture, &c. It is suitable for those who purpose in the future to take any part in the direction of the operations of dyeing or printing of textile fabrics, e.g., the sons of manufacturers, calico printers, managers, master dyers, &c., or in the manufacture of coal-tar products and dye-stuffs.

Leather Industries Department.

Professor—H. R. Procter, M.Sc., F.I.C.

Assistant Professor—E. Stannyn, Ph.D.

Demonstrator—Harold Brumwell.

Research Assistant—S. Hirst.

The full Courses, which extend over a period of either two or three years, are suitable to all who intend to become Technical Chemists in the Leather Industry, or managers of important works, and are recommended to sons of tanners. The Courses include instruction in chemistry, a modern language, leather manufacture, and practical work in the Leather Industries Laboratory and Dye house.

Agricultural Department.

Professor—R. S. Seton, B.Sc.

Lecturer in Agricultural Chemistry—C. Crowther, M.A., Ph.D.

The full Course occupies three years, and includes instruction in chemistry, physics, mathematics, geology, botany, forestry, engineering and surveying, and the principles of agriculture, as well as practical work in the various laboratories and out-door agriculture at the University Farm.

Fuel and Metallurgical Department.

Professor—William A. Bone, D.Sc., Ph.D., F.R.S.

Demonstrator and Research Assistant—H. H. Gray, B.Sc.

The Courses extend over two, three, or four years, and are suitable for those who are preparing for posts either as Gas Engineers or in Fuel and Metallurgical industries.

The Courses in Gas Engineering and the Technology of Fuel will chiefly deal with the manufacture and distribution of coal-gas and gas-lighting problems, by-product coking processes, and the production and application of gaseous fuels for heating and power purposes.

The Metallurgical Courses, besides dealing with general processes for the concentration and extraction of ores, will be chiefly directed to problems underlying blast furnace and open-hearth steel practice, and to the micro-structure, physical properties, and heat treatment of steel and other industrial alloys.

Research Students are admitted to the University Laboratories on reduced terms.

Several valuable Fellowships and Scholarships are at the disposal of the University, including a Fellowship of £100 offered by the Institution of Gas Engineers, and the Salt, Akroyd, Brown, Baines, Emsley, Craven, Leeds City Council, and Clothworkers' Scholarships, and one of the 1851 Exhibition Scholarships. The North, East, and West Ridings County Council's Scholarships are tenable at the University of Leeds.

UNIVERSITY OF LIVERPOOL.

Professor of Chemistry—J. Campbell Brown, D.Sc., LL.D.

Professor of Physical Chemistry—F. G. Donnan, M.A., Ph.D.

Lecturer on Organic Chemistry—A. W. Titherley, D.Sc., Ph.D.

Lecturer on Metallurgy—Guy D. Bengough, M.A., A.R.S.M.

Demonstrators and Assistant Lecturers—A. T. de

Mouilpied, M.Sc., Ph.D.; H. Bassett, D.Sc., Ph.D.; D.es.Sc.; A. Rule, M.Sc., Ph.D.; R. E. Slade, M.Sc.; W. L. Hicks, M.Sc., Ph.D.; and E. G. Jones, M.Sc.

Assistant—H. H. Froyssell.

The Session commences October 4th.

Entrance Scholarship Examination takes place early in May each year.

The Classes meet the requirements of candidates for the Ordinary B.Sc. Degree, for Chemistry Honours, or for the M.Sc. or D.Sc. Degree in the University of Liverpool; for Degrees in Medicine of Liverpool; for the Pharmaceutical, Veterinary, Dental, and Public Health Diplomas; and for those studying Chemistry as a preparation for professional, technical, or commercial life. The Classes qualify for the Fellowship of the Institute of Chemistry and other Examination Boards.

Lecture Courses.

A. General Course on the principal non-metallic elements and the most important metals, the principles of Chemical Philosophy, and an introductory sketch of Organic Chemistry. Three Terms. Fee, £4.

Engineer's Course of Lectures with Practical Class. Two Terms. Fee, including Practical class, £4 10s.

Pharmacy Courses: Junior, £3; Senior, £3.

Course B.—Inorganic Chemistry. Fee, £3.

Course C.—Inorganic Chemistry (Honours Course). Fee, £2 10s.

Course D.—Organic Chemistry. Fee, £3.

Course E.—Organic (Honours). Fee, £4.

Course F.—Physical Chemistry. Fee, £3.

Course G.—Honours Physical Chemistry. Fee, £4.

Course H.—History of Chemistry and Chemical Philosophy. Fee, £2.

Courses J.—Applied Chemistry and Metallurgy: Lectures on Technology are given in connection with Laboratory work at hours to be arranged. The subjects are varied in different years. (1) Alkali and other Inorganic Manufactures, including Fuel and Gas. (2) General Principles of Metallurgy. (3) Iron, Steel, and Aluminium. (4) Copper, Lead, Silver, Gold, and other Metals. (5) Fuel and Illuminating Gas. (6) Technical Gas Analysis. Fee, £2.

Course K.—Applied Organic Chemistry. Fee, £2 10s.

Course L.—Applied Electro-chemistry. Fee, £2 10s.

Practical Classes.

(1) Junior. (2) Intermediate: Qualitative Analysis; preparation of Inorganic Compounds; simple Quantitative and Volumetric Analysis. (3) Revision Class. (4) Engineers' Class. (5) General Metallurgy (Elementary).

Chemical Laboratory.

The Chemical Laboratories provide accommodation for every kind of chemical and metallurgical work and research. They include thirty rooms devoted to the study of General Chemistry, Organic Chemistry, Physical Chemistry, Electro-chemistry, and Metallurgy. Separate rooms are provided for Organic Work, Quantitative Analysis, Water and Gas Analysis, Photometry and Photography, Metallurgy Laboratories, Research Laboratories and Library, and a Museum. Large new Laboratories for Physical Chemistry and Electro-chemistry have been recently erected.

Students desirous of gaining a thorough theoretical and practical acquaintance with Technical Chemistry, or who intend to adopt Chemical work as a profession, must devote three or four years to special study, for which a full curriculum is provided. Fees:—

	One Term, Three Months.	Three Terms One Session.
Per Week		
One day	£4	£7
Two days	5 10s.	10
Three days	7	13
Whole week . . .	10 10s.	21

D.P.H. Course (see special syllabus).

Course for Dental Degree and Diploma (see special syllabus).

Technological Curriculum.

The curriculum extends over three or four years.

The Final Examination for the Associateship of the Institute of Chemistry may be taken after the third year. Those students who have taken the Ordinary Degree of B.Sc. may pass the M.Sc. Exam. in any subsequent year.

The Sir John Willcox Scholarship of £50 per annum, tenable for two years, will be competed for in December, 1908, on an Examination in subjects which are included in the first two and a half years of the above curriculum. Candidates should send in their names to the College Secretary not later than November 15. The Sheridan Muspratt Chemical Scholarship, on similar lines, will be open for competition in December, 1910. Other Scholarships, Entrance Scholarships, and Free Student ships are also available to Students.

Evening Classes.

Classes on Metallurgy will be held during the winter.

Prospectuses containing particulars may be obtained from the Registrar, University of Liverpool.

ARMSTRONG COLLEGE, NEWCASTLE-ON-TYNE

Professor of Chemistry—P. Phillips Bedson, M.A., D.Sc., F.I.C., F.C.S.

Lecturers in Chemistry—F. C. Garrett, D.Sc., F.C.S., and J. A. Smythe, D.Sc., Ph.D., F.C.S.

Assistant Lecturer and Demonstrator—A. A. Hall, M.Sc., Ph.D.

Lecturer in Agricultural Chemistry—S. Hoare Collins, M.Sc., F.I.C., F.C.S.

Assistant to Lecturer in Agricultural Chemistry—H. Crofts, B.Sc.

Demonstrator—A. Forster, B.A.

First Year Courses.—Division I.—This Course of Lectures will extend over the three terms of the Session, and is intended to serve as an introduction to the Science. The Lectures will be of an elementary character, and whilst framed to meet the requirements of First Year Students will also be serviceable to such as intend pursuing Chemistry in its various applications in the arts and manufactures, as, for instance, Brewing, Metallurgy, the Manufacture of Soda, Soap, Glass, &c. The subjects treated will include an exposition of the Principles of Chemistry, and a description of the preparation and properties of the chief Elementary Substances, both metallic and non-metallic, and their more important native and artificial compounds. The class will meet on Mondays, Wednesdays, and Fridays, at 11 a.m., and will commence on Wednesday, October 6th. Fee, £3 10s. for the Session.

Division II. Similar to Division I., but modified to meet requirements of Students for Degrees in Engineering and Mining. Mondays, Tuesdays, and Thursdays, 12 to 1. Fee, £3 10s. for Session.

Second Year Courses.—The Lectures for the second year students consist of a course of Lectures on Organic Chemistry, and a course of Lectures on Inorganic Chemistry. The class on Organic Chemistry will meet on Tuesdays and Thursdays at 11 a.m., and will commence on October 5th. The class for Inorganic Chemistry meets at 11 a.m. on Mondays. Fee for Session, £3 10s.; for Inorganic alone £1 10s.; and for Organic alone £3.

Third Year Courses.—Advanced Classes are held for the study of Inorganic, Organic, and Theoretical Chemistry. Fee for the course, £3 10s.

A Lecture Course in Analytical Chemistry will be given on Fridays, at 9.15 a.m. Fee for the course, £1.

Metallurgy and Assaying.—Lecturer, Prof. Louis, M.A., D.Sc., F.I.C., F.G.S.; Demonstrator, H. Dean, A.R.C.M. A Metallurgical Laboratory is provided, in which instruction is given in the ordinary processes of Dry Assaying, and in the preparation and analysis of Alloys, &c. Fees as for Chemical Laboratory.

Agricultural Chemistry.—The instruction in this branch of Chemistry will consist of a series of Lectures and of special practical work in the Chemical Laboratory.

Students will be expected to have a knowledge of Elementary Chemistry, such as may be obtained by attending the General Course.

The Lecture Course in Agricultural Chemistry is arranged for two days a week throughout the Session. Fee, £3 10s.

Practical Chemistry.—The Laboratory is open from 10 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it closes at 1 p.m. *Laboratory Fees.*—Students working six days per week £5 10s. per term, £15 per session; one day per week, £2 per term, £5 per session.

Courses of Study.—Students will be divided into two classes:—(1) Regular, or Matriculated Students, who are also Members of the University of Durham; and (2) Non-Matriculated Students. Regular Students will be required to follow such a course of study in the subject professed in the College as will enable them to pass the Examinations for the degree of Bachelor in Science of the University of Durham. Non-Matriculated Students will attend such classes as they may select. Every candidate for admission as a matriculated student must have passed the University Matriculation Examination.

The University has recently adopted the following Matriculation Examination for students entering the Faculty of Science:—Additional Mathematics; English; English History; any one subject selected from Religious Knowledge, Botany, Zoology, Physical and General Geography, Experimental Science; any two subjects selected from Latin, Greek, French, German. (Students may substitute Extra Mathematics for one of these optional subjects up to and including September, 1911).

In order to enter on a course of study for a degree in *Engineering Science*, including Mechanical, Civil, and Electrical Engineering, and in Naval Architecture, a student must have previously satisfied the Examiners in the following subjects:—(1) Extra Mathematics, (2) English, (3) English History, (4) General Geography, (5) Experimental Science, (6) one of the following subjects: (i.) Latin, (ii.) Greek, (iii.) French, (iv.) German.

In order to enter on a three years' course of study for a Degree in Letters a student must have previously satisfied the Examiners in the following subjects:—Elementary Mathematics or Additional Mathematics; English; English History; either Latin or Greek; either French or German; one of the following subjects—Religious Knowledge, Botany, Zoology, Physical and General Geography, Experimental Science.

N.B.—(i.). Students who require to take three subjects to qualify for degrees in Science may offer any three of the following:—Additional Mathematics, Extra Mathematics, English, Latin, Greek, French, German, Physical, and General Geography, English History.

(ii.). Foreign Students may be exempted from the Matriculation Examination on report from the Council of the College of Medicine, or from the Board of Professors of Armstrong College, as the case may be, that they have already passed an examination equivalent to the Matriculation Examination of the University, and that they have sufficient knowledge of English to enable them to follow the courses of instruction they are entering for.

(iii.). Students from Oriental countries may be exempted from the Matriculation Examination on report from the Council of the College of Medicine, or from the Professors of Armstrong College, as the case may be, that they have received such an education in their own country as will enable them to profit by University study, and that they have sufficient knowledge of English to enable them to follow the courses of instruction they are entering for.

For detailed Syllabuses and complete Regulations the College Calendar should be consulted.

Bachelorship in Science.—Every candidate for the Bachelorship in Science will be required to satisfy the examiners in Mathematics, Physics, Chemistry, and either Geology or Natural History—in an examination to be held at the end of the candidate's first year, and at the end of the third year in an examination in one chief and two

auxiliary subjects. For details of the subjects the College Calendar should be consulted. Candidates may qualify for the degree of B.Sc. by attending special courses in Agriculture, Engineering, and Mining, and passing the several examinations.

Exhibitions.—Two Exhibitions of the value of £20 and £10 respectively will be awarded in October next to Candidates desirous of attending the first year course of study in the College.

The examination will be held at the College, and will commence on Thursday, September 30th, 1909. Candidates should send in their names to the Secretary on or before September 11th.

Evening Lectures.—Courses of Evening Lectures will be given, with a Practical Class for Laboratory instruction.

Several valuable Scholarships are available for students, including the Johnston Chemical Scholarship of the value of £60 for one year, which is open to Bachelors of Science of any British University; the examination for this Scholarship will be held during the week commencing September 27th. Candidates should send in their names to the Secretary on or before September 19th.

THE UNIVERSITY OF MANCHESTER.

Professor of Chemistry and Director of the Inorganic Laboratories—Harold B. Dixon, M.A., M.Sc., F.R.S.

Professor of Chemistry and Director of the Organic Laboratories—W. H. Perkin, Ph.D., F.R.S.

Senior Lecturers and Demonstrators—Arthur Lapworth, D.Sc.; J. F. Thorpe, Ph.D., F.R.S.; C. Weizmann, Ph.D.; Norman Smith, D.Sc.

Assistant Lecturers and Demonstrators—E. C. Edgar, D.Sc.; H. F. Coward, M.Sc.; Ida Smedley, D.Sc.; J. L. Simonsen, M.Sc.; and Robert Robinson, M.Sc.

Professor of Metallurgy—H. C. Carpenter, M.A., Ph.D.
Demonstrator and Research Fellow in Metallurgy—C. A. Edwards (Carnegie Scholar of the Iron and Steel Institute).

Lecturer in Electro-Chemistry—R. S. Hutton, D.Sc., and J. N. Pring, M.Sc.

The Session begins October 5, 1909.

The Chemical Classes form part of the Courses for Degrees in the University.

Chemistry Lecture Courses.

General Chemistry Course.—Tuesdays, Thursdays, and Saturdays, at 9.30, during the two Winter Terms.

Introduction to Organic Chemistry.—Wednesdays and Fridays, at 9.30, during the Lent Term.

These courses are intended for Students commencing the study of chemistry.

First Year Honours Course.—Mondays, Wednesdays, and Fridays, 11.30, during the two Winter Terms. The Non-Metals.

Second Year Honours Course.—Mondays, Wednesdays, and Fridays, at 2, during the two Winter Terms. The Metals.

Third Year Honours Course.—Theoretical and Physical Chemistry.

Organic Chemistry (General).—Mondays and Fridays, at 9.30, during the two Winter Terms.

Organic Chemistry (Advanced).—Tuesdays and Wednesdays, at 9.30, during the two Winter Terms.

History of Chemistry.—Short Courses during the two Winter Terms.

Metallurgy.—Introductory Course, followed by either—(A) Lead, Copper, Bismuth, Antimony, Zinc, and Tin; or (B) Iron and Steel. Each Course, one Lecture per week during the Session.

Electro-chemistry.—General Theoretical Course: Two hours per week during the Michaelmas Term.

Certificate in Applied Chemistry.—The course extends over three years, and comprises systematic instruction by means of lectures and practical work in the laboratories.

For further particulars of any of these courses apply to the Registrar, Edward Fiddes, M.A.

UNIVERSITY COLLEGE, NOTTINGHAM.

DEPARTMENTS OF CHEMISTRY AND METALLURGY.

Professor of Chemistry—F. Stanley Kipping, Ph.D., D.Sc., F.I.C., F.R.S.*Demonstrators of Chemistry*—R. M. Caven, D.Sc., F.I.C.; G. Sand, D.Sc.; and G. Martin, Ph.D., B.Sc.

The Classes of the College are open to students of both sexes above sixteen years of age.

The Session commences in October, for both Day and Evening Classes.

Lecture Courses.—The Chemistry Day Lectures extend over three years. In the first year a student enters for the course on Elementary Chemistry. In his second year he attends Lectures on both Inorganic and Organic Chemistry. In his third year he attends courses on Advanced Organic Chemistry, Physical Chemistry, and Advanced Inorganic Chemistry.

The fees for the Day Lectures and Classes are as follows: First year, two Lectures per week, 15s. per term. Second year, three Lectures per week, 22s. 6d. per term. Third year, four Lectures per week, 30s. per term.

Demonstrations and Lectures on Analytical Chemistry are given, and Chemical Calculation and Tutorial classes are also held. Various short courses of lectures on special subjects are delivered during the Session.

Students may qualify themselves by attendance at these lectures and classes for the Examinations of the Universities of London, Cambridge, or Oxford, and for the Medical Examinations of the Royal College of Surgeons and of the Universities of Cambridge and Edinburgh: they may also obtain instruction in Chemistry for technical or other purposes, and can enter for a full Chemical Engineering Curriculum. Special attention is given to the requirements of candidates for the Associateship of the Institute of Chemistry.

Practical Chemistry and Metallurgy.—The Chemical and Metallurgical laboratories are open every day from 9 to 5, except on Saturday, when the hours are from 9 to 1; also on Tuesday and Thursday evenings from 7 to 9. Each Student works independently of other Students at a course recommended by the Professor. Instruction is given in general Chemical Manipulation, in Qualitative and Quantitative Analysis, and in the methods of Original Chemical Investigation and Research; Students are also enabled to work out the applications of Chemistry to Pharmacy, Metallurgy, Dyeing, Agriculture, Brewing, Iron and Steel, Tanning, and other Manufacturing Processes. Fees for day students: For one term, £7; for the session, £18; for six hours weekly 40s., and 15s. extra for each additional hour per week. Evening students, 10s. for 2 hours per week, 3 hours 15s., 4 hours 20s., per term.*Research Work.*—Students or others wishing to undertake research work in pure or Applied Chemistry will be afforded every facility for doing so and may be admitted at reduced fees. The Laboratories are fully equipped with apparatus and chemicals necessary for such work.*Courses of Technical Chemistry Lectures* are also given on Engineering, Dyeing and Bleaching, Brewing, Plumbing, Bread-making, Gas Manufacture, and on other processes of applied Chemistry.*Pharmaceutical Students* are provided with Lectures and Laboratory work suitable for the preparation for the Minor and Major Examinations.*Evening Classes.*—Evening Lectures and Laboratory instruction will be given in Pure and Applied Chemistry, and the laboratories are open for practical work on Tuesday and Thursday evenings from 7 to 9. Fee for each Lecture Course, 5s.; for each Laboratory Course, 10s.

Full information concerning all College Classes is given in the College Prospectus, free from the Registrar.

THE UNIVERSITY OF SHEFFIELD.

Professor of Chemistry—W. P. Wynne, D.Sc., F.R.S.*Lecturers and Demonstrators*—W. E. S. Turner, M.Sc., B.Sc.; W. J. Jarrard, B.Sc.; C. R. Young, B.Sc.

The Session will commence October 6th.

Matriculation Course.—Tuesday and Friday at 9.30. Fee, £2 12s. 6d., and three hours per week Laboratory work.

Candidates for the Intermediate Examination are required to satisfy the Examiners in three of the following subjects:—Pure Mathematics, Applied Mathematics, Physics, Chemistry, and Biology. And those for the Final Examination in three of the following subjects:—Pure Mathematics, Applied Mathematics, Physics, Chemistry, Zoology, Botany, Physiology, Geology, Education.

Intermediate Course in Chemistry for B.Sc. or M.B.—Monday, Tuesday, Thursday, and Friday at 9.30 a.m. £5 5s., and six hours per week Laboratory work.*B.Sc. Course in Chemistry.*—Monday at 9.30 a.m. and 12.30 p.m., Wednesday at 11.30 a.m., and Thursday at 10.30 a.m. and 12.30 p.m., £4 4s., and nine hours per week Laboratory work during two Sessions.*B.Sc. with Honours.*—Honours Students in Chemistry, after passing the Intermediate Examination, devote the whole of their time to the study of Chemistry, and are expected to reach the standard for a pass in Chemistry for the ordinary degree by the end of the second year. During the second or third year they devote one day a week to lectures and practical work in a subsidiary subject—Mathematics, Physics, or Metallurgy—selected for the degree. The third year is devoted to the advanced study of Chemistry, either chiefly Physical and Inorganic or chiefly Organic, as the student may select. At least four days a week during the second and third years are spent in the laboratory.*M.Sc.*—This degree may be conferred upon a Bachelor of Science with Honours who is of one year's standing from the date of his graduation as a Bachelor of Science, or upon any Bachelor of Science who has either passed an examination in an Honours School subsequent to graduation, or has for at least one year after graduation done research work at the University, and has presented a thesis, approved by the Faculty of Pure Science, upon the research work done during that period.*D.Sc.*—The degree of Doctor of Science may be conferred upon any Master of Science of not less than five years' standing from the date of his admission to the degree of Bachelor, provided that he has published, in recognised journals or transactions, a research or researches of special merit and approved by the Faculty of Pure Science as qualifying him for the degree.*Laboratory.*—Working hours to be arranged between Professor and Students.

Sessional Fees for Day Students:—Three hours per week, £3 3s.; Six, £5 5s.; Nine, £7 7s.; Twelve, £9 9s.; Eighteen, £12 12s.; Twenty-four, £14 14s.; Thirty-two, £16 16s.; Honour or University Students taking eighteen hours or more per week, £12 12s.

Students joining the Laboratory at Christmas will be charged two-thirds and at Easter one-third of the Fees for the whole Session.

A Course of Lectures, with a special class in Laboratory Work, is arranged for Medical Students entering for the Conjoint Board Examinations. Fee, £7 7s.

A course of Elementary Practical Physics and Practical Chemistry, which will meet the requirements of candidates for the Diploma of Public Health is held during the Michaelmas and Lent terms. Fee £5 5s.

An arrangement has been entered into with the Board of Education, South Kensington, which will enable Science Teachers to work in the Chemical Laboratory for three, six, or twelve hours a week on payment of one-quarter of the usual fee, the Board being willing to pay the remainder under certain conditions, of which full information may be obtained on application to the Registrar of the University.

Evening Classes.—Lecture Class and Laboratory, on Wednesday evening during the Michaelmas and Lent terms. Fee, £1 10s.

DEPARTMENT OF METALLURGY.

Professor—J. O. Arnold, D. Met.*Assistant Professor*—A. McWilliam, M. Met. A.R.S.M.

This Department has been equipped to meet the requirements of the local industries. The Laboratory is fitted with the most modern apparatus for metallurgical analysis, more especially with appliances for the rapid and accurate chemical examination of Iron and Steel, Fuel, and Refractory materials. It also contains a complete pyrometric installation, and a laboratory for the study of the micrographic analysis of metals fully equipped with specially designed microscopes by Ross, polishing tables, etching appliances, incandescent light for evening work, &c. The School is now the most complete of its kind for teaching the practical manufacture, the chemical constitution, and the physical properties of Steel. Special attention is given to the determination of the microscopic constituents of Steel. Although the chief industry of the district occupies the central position in the course of instruction, general metallurgy is not neglected, but is dealt with in a separate syllabus, dealing with metals (other than iron and steel) used in the arts. Students are thus enabled to select and at once enter upon a course of scientific metallurgical training of immediate practical utility. They may take up and work through any portions of the course, but certificates will be granted only to those who follow the prescribed courses, and pass the necessary examinations. Lectures on Iron and Steel Manufacture, on Fuel and Refractory Materials, and on General Metallurgy. Practical Metallurgy:—Laboratory, Furnaces, Foundry, and Testing Machine Course; Practical Course of Metallurgy other than Iron and Steel; Practical Fuel Course for Students in Collieries or Gas Works.

A new steel works has recently been erected in connection with the Sheffield University at a cost of about £15,000. The works include a two-ton open-hearth furnace, a one-ton Bessemer plant, and a four-hole crucible melting plant. The works are also provided with a hammer capable of dealing with four-inch ingots. Differential annealing furnaces and gas and electric hardening furnaces constitute part of the new plant. Additional laboratory accommodation is attached to the works, viz., chemical laboratory for staff, chemical laboratory for post graduate students, together with a complete magnetic laboratory for hysteresis, &c.

The most recent addition to the steel works plant is a 3 cwt. Kjellin induction furnace worked by a 120 H.P. Motor-generator set with two-phase current. The Metallurgical Department of Sheffield University is (subject to an order by the King in Council) "in association" with the Royal School of Mines for teaching the advanced metallurgy of Iron and Steel.

UNIVERSITY COLLEGE, DUNDEE.

UNIVERSITY OF ST. ANDREWS.

Professor of Chemistry—Hugh Marshall, D.Sc., F.R.S.

Assistant Lecturers—J. K. Wood, D.Sc. and (Vacant).

Lecture Assistant and Lab. Steward—J. Foggie, F.C.S.

The Winter Session begins early in October and ends in March. The Summer Session extends from the middle of April to the end of June.

The *Junior Lecture Course on Systematic Chemistry* is given daily during the Winter Session, and embraces the Elements of Inorganic and of Organic Chemistry.

Advanced Courses, of about fifty lectures each, will be given during the year as follows:—

Organic Chemistry; Inorganic Chemistry, including the more important technological applications; Theoretical and Physical Chemistry; Bleaching and Dyeing, including the Chemistry of the Textile Fibres.

Practical Instruction in all of the above branches will be given in the Laboratories and Dye-house. Special facilities are afforded to Research Students.

UNIVERSITY OF ABERDEEN.

CHEMISTRY.

Professor—Francis R. Japp, M.A., LL.D., F.R.S.

Demonstrators—Francis W. Gray, M.A., D.Sc., and Joseph Kn. x, D.Sc.

I. *General Lecture Course (100 Lectures)*.—Daily during

the Winter Session. The subjects treated of include (1) The Laws of Chemical Combination and the General Principles of Chemistry; (2) Non-metallic and Metallic Elements, and their Compounds; (3) Organic Chemistry; (4) Applications of Chemistry to the Arts and Manufactures. Fees, for first attendance, £4 4s.; for subsequent attendance, £3 3s. A Tutorial Class (without fee), conducted by the Junior Demonstrator, is held in connection with this course.

II. *Physical Chemistry (60 Lectures)*.—Three Lectures a week on Physical Chemistry are delivered during the Winter Session by the Lecturer, Dr. F. W. Gray. Fee, £2 2s.

III. *Inorganic Chemistry (40 Lectures)*.—Two Lectures a week on Advanced Inorganic Chemistry are delivered during the Winter Session by the Lecturer, Dr. J. Knox. Fee, £2 2s.

IV. *Special Lecture Course on Organic Chemistry (50 Lectures)*.—Daily during the Summer Session. Fee, £3 3s.

V. *Practical Course for Medical Students*.—This course, which occupies five hours a week during the Summer Session—in all fifty hours—is devoted to practice in Elementary Qualitative Analysis. Fee, £3 3s.

VI. *Chemical Laboratory*.—The Laboratory is open to Students daily from 9 a.m. to 5 p.m. Each Student on entering is allowed to arrange his hours of work so as to suit his own convenience, but must adhere to these hours when once fixed. The Laboratory instruction includes: (1) General experiments; (2) Preparations; (3) Qualitative analysis; (4) Quantitative analysis: gravimetric, volumetric, and gasometric. The Course qualifies for the examinations of the Institute of Chemistry. Fee, £3 3s. a session. A certain number of free places are available, on the recommendation of the Professor, and subject to the approval of the Senatus, for research students.

UNIVERSITY OF ABERDEEN AND ABERDEEN AND NORTH OF SCOTLAND COLLEGE OF AGRICULTURE.

Agricultural Chemistry.

Lecturer—James Hendrick, B.Sc., F.I.C.

Assistants—R. Glegg, B.Sc., F.I.C.; A. J. Findlay, M.A., B.Sc. (Agr.), N.D.A., N.D.D.

I. *Preparatory Courses in General Chemistry and in Organic Chemistry* are given for those who are unable to take the full University Courses in these subjects. The course in General Chemistry consists of about sixty Lectures with Practical Work (one hour daily) during the Winter Session. The course deals with the general principles of Chemistry, and with those parts of Inorganic Chemistry which are of more immediate concern to students of Agricultural Chemistry. The Practical Work goes along with and illustrates the Lectures. Fee, £4 4s.

The course in Organic Chemistry consists of about thirty Lectures, and is given during the Winter Session. It deals especially with those parts of the subject which are directly related to Agricultural Chemistry. Fee, £1 1s.

II. *Agricultural Chemistry (General Course)*.—This class meets daily during the Winter Session, and includes both Lectures and Laboratory Work. The Lectures deal with the Chemistry of the Atmosphere, the Soil, Manures, Foods, Preservatives, Insecticides, &c. The Physiological Chemistry of Plants and Animals, the Composition and Manurial Requirements of Crops, and Dairy Chemistry are also treated of. The Laboratory Work is primarily intended to accompany and illustrate the Lectures. Exercises dealing with the properties and composition of Soils, Manures, Feeding-stuffs and Waters, and with the impurities and adulterations of these, occupy much of the time given to Practical Work. The fee for the whole Course (Lectures and Practical Work) is £4 4s.

III. *Laboratory*.—A Summer Course in Practical Chemistry is given to prepare students who have not previously done sufficient laboratory work for the course in Agricultural Chemistry. Fee, £2 2s.

IV. The Laboratory is open daily from 9 a.m. to 5 p.m. for students who wish to study the principles and practice

of Agricultural Chemistry or to undertake research in this subject.

UNIVERSITY OF EDINBURGH.

DEPARTMENT OF CHEMISTRY.

Professor—James Walker, D.Sc., Ph.D., F.R.S.

Lecturers—L. Dobbin, Ph.D.; A. C. Cumming, D.Sc.; W. W. Taylor, M.A., D.Sc.; and J. E. Mackenzie, Ph.D., D.Sc.

The working terms are—Winter Session, from beginning of October to middle of March; Summer Session, from beginning of May to middle of July.

Lecture Courses.—During the Winter Session a General Course of Chemistry for medical students is given by the Professor. The class meets daily; fee, £4 4s. The First Course for Arts and Science students is given by Dr. Dobbin. The class meets three times a week throughout the year (Summer and Winter Sessions); fee, £4 4s. The Second Course is given by the Professor on Organic, Advanced Inorganic, and Physical Chemistry. The class meets three times a week throughout the year; fee, £4 4s. Tutorial Classes are held in connection with both First and Second Courses. All Arts and Science Classes are open to Women Students.

In addition to the above, Lecture Courses are from time to time given by the Assistants on particular branches of Physical, Organic, and Inorganic Chemistry.

Laboratories.—Practical classes for Medical Students meet during the Winter Session and in the Summer Session. (Fee, £3 3s.) The laboratories for Science and Arts Students engaged in analytical and advanced practical work are open daily from 9.30 till 4.30. (Fees: Whole Day—Winter Session, £10 10s.; Oct.-Dec., Jan.-March, or Summer Session, £5 5s. Half Day—Winter Session, £6 6s.; Oct.-Dec., Jan.-March, or Summer Session, £3 3s. Preference will be given to students in the above order.) Full Courses of instruction are given in Analytical, Practical Organic and Inorganic Chemistry (including Gas Analysis), Physico-chemical Measurements, Agricultural Chemistry, and Assaying. Facilities are afforded to advanced students who desire to undertake chemical investigations.

Various prizes and scholarships are attached to the laboratory and general class.

Graduation.—Two Degrees in Pure Science are conferred, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.).

Candidates for Degrees in Science, if not graduates (by examination) in Arts in one of the Universities of the United Kingdom or in a Colonial or Foreign University recognised for the purpose by the University Court, must pass a preliminary examination in (1) English; (2) Latin, Greek, French, or German; (3) Mathematics; (4) One of the languages Latin, Greek, French, German, Italian, not already taken under (2), or Dynamics. In the case of a student whose native language is other than European, the Senatus may, at the Preliminary Examination, accept such language as a substitute for a modern European language. The Senatus may also in such a case accept as an alternative to Latin or Greek any other classical language, such as Sanscrit or Arabic.

The First B.Sc. Examination embraces Mathematics, or Biology (*i.e.*, Zoology and Botany), Natural Philosophy, and Chemistry. The Final B.Sc. Examination in Pure Science includes any three or more of the following subjects:—Mathematics, Natural Philosophy, Astronomy, Chemistry, Human Anatomy (including Anthropology), Physiology, Geology (including Mineralogy), Zoology (including Comparative Anatomy), and Botany (including Vegetable Physiology). In the Final Examination two written papers are set in each subject professed, the second of a higher standard than the first. Candidates must pass the first section in all, and the second section in at least one, of the subjects professed; the same regulations apply also to the Practical and Oral Examinations. Chemistry in this examination embraces Inorganic, including Mineralogical, Chemistry; Organic Chemistry; Physical Chemistry;

Chemical Crystallography; History of Chemistry. In the written papers a choice of questions is allowed, so as to adapt the examination to the various courses of advanced study which candidates may have selected. Practical Examination:—Complex Qualitative Analysis; Inorganic Preparations; Gravimetric and Volumetric Analysis. Each candidate taking the higher standard will also be examined on Organic Preparations, Ultimate Organic Analysis, and one of the following subjects, selected by himself:—Gas Analysis; Assaying; Physico-chemical Measurements, including Practical Crystallography as a special branch.

A candidate for the D.Sc. Degree must submit a thesis on original work done by him. The Thesis must be approved before the candidate is allowed to proceed to Examination. The candidate in Chemistry may be required to pass a searching examination in one of the following branches:—(1) The Chemistry and Chemical Technology of Inorganic Bodies, including Metallurgy; (2) Organic Chemistry; and to show a thorough practical acquaintance with chemical analysis in all its branches, and with the preparation of pure substances.

HERIOT-WATT COLLEGE, EDINBURGH.

Principal—A. P. Laurie, M.A., D.Sc., F.R.S.E.

Professor—John Gibson, Ph.D., F.R.S.E.

Assisted by the following Lecturers and Demonstrators:—R. B. Denison, D.Sc., Ph.D.; Archibald Boon, B.A., B.Sc.; Andrew F. King, F.I.C.

The Session begins Sept. 27th, 1909.

The curriculum of this College comprises both Day and Evening Classes, each department providing the higher general and technical education.

The Chemistry Course is designed to meet the wants of Manufacturing Chemists. The instruction consists of Courses in Chemistry, Physics, Mathematics, Engineering, and Mechanical Drawing, with Special Courses in Gas and Paper Manufacture, Brewing, &c., by Experts, in the fourth year. Special attention will be paid to Electro-chemistry. The Chemistry Classes are recognised by the University as qualifying for the B.Sc., in Chemistry, and are also recognised by the Institute of Chemistry.

For Students who have been three and four years in the Chemistry Department, arrangements have been made for their spending from four to twelve months in the laboratories of the Corporation's Gas Works, with a view to the study of problems connected with the Combustion of Fuel, the Manufacture of Coal-gas and its By-products, &c.

A Laboratory, under the charge of Dr. Emil Westergaard, has been provided for the study of Technical Mycology, including Brewing, Distilling, Malting, Vinegar Making, Tanning, Preserving, Starch and Sugar Making, Bread Making, Butter and Cheese Manufacture, &c.

Matriculation Fee, 5s.; Composition Fees from £12 12s. to £15 15s. Full particulars are published in the Calendar of the College, which is issued early in September.

GLASGOW AND WEST OF SCOTLAND TECHNICAL COLLEGE.

Professor of Chemistry—G. G. Henderson, D.Sc., M.A.

Professor of Technical Chemistry—T. Gray, D.Sc., Ph.D.

Lecturer on Metallurgy—A. Campion, F.I.C., F.C.S.

Also, Professors and Lecturers in the other leading branches of Pure and Applied Science and Technology.

Session opens Sept. 28.

The main objects of this College are to afford a suitable education to those who wish to qualify themselves for following an industrial profession or trade, and to train teachers for technical schools. It was founded by an Order in Council, dated 26th November, 1886, according to a scheme framed by the Commissioners appointed under the provisions of the Educational Endowments (Scotland) Act, whereby Anderson's College, the Young Chair of Technical Chemistry in connection with Anderson's College, the College of Science and Arts,

Allan Glen's Institution, and the Atkinson Institution were placed under the management of one governing body.

The Diploma of the College is awarded to Day Students who have attended prescribed courses of instruction and passed the necessary examinations. The ordinary courses extend over three years, but arrangements are made for advanced students continuing their studies in special departments. The diploma course in Chemistry extends over four years.

Complete courses of instruction are provided in both Day and Evening Classes.

Copies of the Calendar for 1909-1910 may be had from Mr. H. F. Stockdale, Secretary; price by post, 1s. 4d. Prospectuses will be sent free.

UNIVERSITY OF ST. ANDREWS.

UNITED COLLEGE OF ST. SALVATOR AND ST. LEONARD.

Professor of Chemistry—James C. Irvine, Ph.D., D.Sc.

The Session begins on October 6th. A Competitive Examination, open to intending Students of Arts, Science, and Medicine, for about thirty-seven Bursaries, ranging in value from £40 to £10 each per annum, will be held on September 10th and following days. Twenty-two of these Bursaries are restricted to Men, one is open to Men or Women, and fourteen are restricted to Women, the latter being intended for women who at the conclusion of their Arts or Science Course will proceed to Medicine.

A Hall of Residence is provided for Women Students.

Two Degrees in Science are conferred by the University of St. Andrews, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.), and Chemistry is also included in the curriculum for the M.A. Degree, and the M.B., Ch.B. Degrees; the regulations will be found in the "University Calendar."

Lecture Courses.

Two distinct Courses of Lectures are given, each comprising at least one hundred meetings of the class.

First Year's Course.—This Class meets at 11 o'clock on five days in the week. The introductory lectures treat of the Nature of Chemical Action, the Classification of Substances into Elements and Compounds, the Phenomena of Oxidation, and the Composition of Air and Water. The Laws of Chemical Combination and the Atomic Theory are next discussed, after which the more commonly occurring elements and inorganic compounds are described systematically. Elementary Organic Chemistry is also included in the Course.

The chemistry of manufactures is referred to only cursorily; special attention, on the other hand, is given to those parts of the science which are of general educational value, and as much of the theory of chemistry is introduced as is compatible with elementary treatment.

This course of instruction is intended to meet the requirements of the M.A., First Science, and M.B., Ch.B. Exams., so far as Theoretical Chemistry is concerned.

Second Year's Course.—The first part of the Course is devoted to Organic Chemistry, and the second part to General and Physical Chemistry, the instruction in general being such as is required for the Final Science Exam.

Certificates are awarded on the results of examinations, and the "Forrester Prize" of about £10 is awarded to the best Student of the year.

Fee for the Session, for each Course, £4 4s.

Practical Chemistry.

The Laboratory is open daily from 9 a.m. to 4 p.m., except on Saturdays, when it is closed at 1 p.m. The work pursued in the Laboratory comprises:—(1) The performance of experiments illustrative of the Principles of Inorganic and Organic Chemistry; (2) Qualitative and Quantitative Analysis. Each student pursues an independent course of study under the supervision of the Professor or Demonstrator, the nature of the work varying with the proficiency of the student and the particular object he may have in view. Suitable courses of

instruction in Practical Chemistry are provided for candidates for the Exams. in Arts, Science, and Medicine.

The fee for the Ordinary Course of Practical Chemistry is £3 3s, and for the Advanced Course £5 5s.

Original Research.

A special Research Department has been instituted by the University, the laboratories of which are open to students who give proof of their capacity of conducting original investigation. Graduates of other Universities who spend two years in the laboratory as Research Students are eligible for the D.Sc. degree of the University, and, as far as possible, special chemicals and apparatus are provided free of charge.

Students may work either independently or in collaboration with the Professor, to whom all communications should be addressed.

QUEEN'S COLLEGE, BELFAST.

Professor—E. A. Letts, Ph.D., D.Sc., F.R.U.I., &c.

I.—*Chemistry.*—The lectures are delivered at 3 p.m., on the first five days of each week, and terminate at the end of March. The course is divided into three parts:—(1) Chemical Philosophy; (2) Inorganic Chemistry; (3) Organic Chemistry. Fee, £2.

II.—*Practical Chemistry.*—In this course the Students are instructed in the general methods of conducting Chemical Analyses. Fee, £3.

III.—*Laboratory Pupils.*—The Chemical Laboratory is open from November until the end of March, and from May 1st until the third week of July, on the first five days of the week, from 10 a.m. until 4 p.m. Students are admitted as working pupils on payment of a fee of £5 for the first period, or of £3 10s. for the second period (or for a single term).

Scholarships.—The following College Scholarships are awarded specially in connection with the schools of Chemistry and Physics:—Senior Scholarships in Chemistry alone awarded annually of £40, and tenable for one year. Andrews Studentship in Chemistry and Physics, value about £80 annually, and tenable for two years. 1851 Exhibition Scholarships: One of these Scholarships has hitherto been placed at the disposal of the College every two years, of the annual value of £150, tenable for two or under special conditions for three years.

The following Scholarships, &c., of the Royal University of Ireland are awarded in the same group of subjects (Chemistry and Physics):—At the B.A. Degree examination, First-class Exhibitions of £42 each and Second-class Exhibitions of £21. At the M.A. Degree examination, a Studentship of £100 per annum, tenable for three consecutive years. Also a Junior Fellowship, tenable for four years, of the annual value of £200.

UNIVERSITY COLLEGE, CORK.

Professor—Augustus Edward Dixon, M.D.

Demonstrator—John Taylor, M.Sc.

The College Session will commence in October, 1909, and end in June, 1910. All classes are open to male and female students.

The courses in Chemistry, though designed primarily to meet the requirements of candidates proceeding to the Examinations in Arts, Medicine, and Engineering of the National University of Ireland, of the Medical Licensing Bodies of Dublin and Edinburgh, and of the Pharmaceutical Society of Ireland, can be arranged specially as required, so as to render them suitable to any particular course of study. The following courses are provided:—

Systematic Chemistry.

I. General Lecture Course; three terms. Inorganic Chemistry, Elementary Organic Chemistry, and Chemical Philosophy.

II. Advanced Organic Chemistry, and Chemical Philosophy.

Practical Chemistry.

III. Winter Course of Practical Analytical Chemistry; commencing early in January, 1908.

IV. Summer Course of three months' duration, for students of Medicine; ending about the third week in June.

V. Course for Pharmaceutical Students; held during the second and third terms.

Laboratory Work.

VI. The Chemical Laboratory is open daily from 10 to 4 o'clock, except on Saturdays, to Students entering for Special Courses of practical work in General Inorganic Chemistry, Qualitative and Quantitative Analysis, Organic Chemistry, or for the purpose of Original Investigation.

Scholarships, &c.—In addition to the Class Prizes given at the Sessional Examinations, the College awards a Senior Scholarship of the value of £40, for Chemistry and Physics (either of which may be taken as a limited course), and numerous Junior Scholarships in Arts, Medicine, and Engineering, of which chemistry forms a part, value from £20 to £24 each, annually; and the 1851 Exhibition Scholarships, value £150, tenable for two, and, under certain circumstances, for three years, have from time to time been placed at the disposal of the College.

Full particulars as to Lectures, Fees, Scholarships, Exhibitions, &c., are contained in the Regulations extracted from the College Calendar, which will be supplied on application to the Registrar.

UNIVERSITY COLLEGE, GALWAY.

NATIONAL UNIVERSITY OF IRELAND.

Professor—Alfred Senior, Ph.D., M.D., D.Sc., F.I.C., F.C.S., M.R.I.A.

Demonstrator—Arthur Compton, B.A., M.B.

Research Assistant—Frederick G. Shephard, B.Sc., &c.

The Session commences in October and ends in June.

Chemistry is studied by attendance at Lectures, by work in the Laboratories, and by the use of the College Library. The Courses in the several faculties are arranged in accordance with the requirements of the University, but are adapted also to those of other Universities and licensing bodies.

Lecture Courses. Faculty of Arts.—1. Second year's Course, Inorganic and Organic, and the Elements of General Chemistry. 2. Third year's Course, Advanced Organic Chemistry. 3. Fourth year's Post-Graduate Course, Advanced General Inorganic and Organic Chemistry. *Faculty of Medicine.*—First year's Course, Inorganic and Elementary Organic Chemistry. *School of Engineering.*—First year's Course, Inorganic Chemistry.

Laboratory Courses. Faculty of Arts.—1. Second year's Course, Exercises in Inorganic Qualitative Analysis. 2. Third year's Course, Quantitative Analysis and other experiments to suit the requirements of individual Students. 3. Fourth year's Post-Graduate Course, Advanced Quantitative Analysis, Organic and Inorganic Preparations, and determination of their Physical and Chemical characters. 4. The Laboratories are also open to Students for work in other branches of Chemistry. *Faculty of Medicine.*—1. Second year's Course, Inorganic and Organic Elementary Qualitative Analysis, and the Chemical Examination of Urine. *School of Engineering.*—1. Second year's Course, Inorganic Qualitative Analysis.

A Scholarship in Chemistry is offered for competition each year of the value of £40, and Chemistry enters into the subjects required for numerous Scholarships in Arts, Medicine, and Engineering. The Royal Commissioners for the Exhibition of 1851 offer every two years a Science Research Scholarship of £150 per annum. This Scholarship has already been held by six Chemistry Students of this College.

For details as to Fees, Regulations as to Scholarships, and other particulars apply to the Registrar, from whom the Calendar, published in December, and the Extracts from Calendar, published in advance in July, may be obtained.

ROYAL COLLEGE OF SCIENCE, DUBLIN.

Dean of Faculty and Professor of Chemistry—W. N. Hartley, F.R.S., D.Sc.

Lecturer on Organic Chemistry—Alphonsus O'Farrelly, M.A.

Senior Assistant—J. Holms Pollok, D.Sc.

Junior Assistant—J. Ivon Graham, A.R.C.Sc.I.

The Royal College of Science supplies, as far as practicable, a complete course of instruction in Science applicable to the Industrial Arts, and is intended also to aid in the instruction of teachers for the local Schools of Science.

Diplomas are awarded in the Faculties of Engineering (Mechanical and Electrical), Applied Chemistry, and Agriculture. If accompanied by a certificate from the Professor of Chemistry, the Diploma of Associate of the Royal College of Science in the Faculty of Applied Chemistry is recognised by the Council of the Institute of Chemistry of Great Britain and Ireland as qualifying candidates for admission to the practical examinations of the Institute.

The instruction in Chemical Science includes (1) General Chemistry; (2) Organic Chemistry, Elementary and Advanced; (3) Analytical and Experimental Chemistry; (4) Instruction in Chemical Research.

Fees payable by Non-Associate Students:—£2 for each separate Course of Lectures. For Analytical Chemistry and Research—£5 for three months; £9 for six months; £12 for the entire session. Assaying—£5 for three months; £9 for six months. £12 for the entire session.

There are four Royal Scholarships of the value of £50 each yearly, with Free Education, including Laboratory Instruction, tenable for two years; two become vacant each year; they are awarded on the results of their examinations to Associate Students, not being Royal Exhibitioners, who have been a year in the College.

A limited number of Scholarships in Science and Technology are competed for each year. These Scholarships are of the value of £50 a year for three years, and, in addition, entitle the holder to free instruction during the full Associateship Course.

For further particulars apply to the Registrar.

PROFESSIONAL CHEMICAL QUALIFICATION (F.I.C. AND A.I.C.).

THE INSTITUTE OF CHEMISTRY OF GREAT BRITAIN AND IRELAND.—The Institute of Chemistry was founded in October, 1877, and incorporated by Royal Charter in June, 1885, (i.) to promote the better education of persons desirous of becoming professional consulting and technological chemists, public analysts, and chemical advisers; (ii.) to examine Candidates, and to grant certificates of competency; and (iii.) to elevate the profession of Consulting and Analytical Chemistry by setting up a high standard of scientific and practical proficiency and by insisting on the observance of strict rules in regard to professional conduct. *The Studentship.*—Every Candidate for admission to the Studentship is required to produce evidence that he is at least seventeen years of age, and that he has passed a Preliminary Examination in subjects of general education, recognised by the Council of the Institute. He must also show that, at the time of making application for registration, he is working at a College or University recognised by the Council, or under the direction of a Fellow of the Institute in an approved laboratory. *The Intermediate Examination in General Theoretical and Practical Chemistry.*—Candidates for admission to the Intermediate Examination are required to produce evidence (I.) of having passed an approved Preliminary Examination in subjects of general education; (II.) of having regularly attended systematic day courses, in a College or University recognised by the Council, during at least three academic years, in theoretical and practical Chemistry, and courses in Physics, Mathematics, and one of the following subjects, in accordance with the Regulations of the Institute: (i.) Higher Physics; (ii.) Advanced Mathematics; (iii.) Mechanics and Chemical Engineering; (iv.) Metallurgy; (v.) Geology and Mineralogy; (vi.) Physiology; (vii.) Bacteriology; (viii.) Agriculture; (ix.) Elementary Botany; (x.) Elementary Biology; and (III.) of having satisfactorily passed the

Class Examinations in all the subjects required to be taken. As an alternative in the matter of training (II.) a candidate may take two years' day courses in a recognised Institution as indicated above, and work systematically for two other years under a Fellow of the Institute in an approved laboratory. A Candidate who has taken a Degree in Science (including Inorganic and Organic Chemistry, and Physics in the Degree Examination, Mathematics having been also passed in at either the Final or Intermediate University Examination) in a University recognised by the Council, is eligible for admission to the Intermediate Examination of the Institute. Holders of certain Honours Degrees or Diplomas are exempt from passing the Intermediate, and, by virtue of their qualifications, are eligible for admission to the Final Examination direct. *The Final Examination for the Associateship (A.I.C.).*—This comprises, in addition to a general knowledge of all branches of chemistry, a thorough knowledge of one branch—mineral chemistry; metallurgical chemistry, physical chemistry, organic chemistry, chemistry of food and drugs and water (including a compulsory examination in therapeutics, pharmacology, and microscopy), or biological chemistry. Any Candidate who has passed the Intermediate Examination of the Institute, or who is entitled to claim exemption from passing the Intermediate Examination, is eligible for admission to the Final Examination. *Fellowship (F.I.C.).*—For admission to the Fellowship, an Associate is required to have been registered for three years, and to have been continuously engaged during that period in the study and practical work of applied chemistry in a manner satisfactory to the Council. Full particulars are given in "The Book of Regulations for the Admission of Students, Associates, and Fellows," which may be obtained (Price One Shilling) from the Registrar, 30, Bloomsbury Square, London, W.C.

CHEMICAL LECTURES, CLASSES, AND LABORATORY INSTRUCTION.

CITY AND GUILDS OF LONDON INSTITUTE FOR THE ADVANCEMENT OF TECHNICAL EDUCATION.—The operations of the City and Guilds of London Institute are divided broadly into four branches: the educational work of three London Colleges, and of the Technological Examinations. Programmes of the London Colleges may be had on application to the Head Office of the Institute, Gresham College, Basinghall Street, London, E.C., or from the respective Colleges. The Technological Examinations (Examinations Department, Exhibition Road, S.W.), are conducted once every year at various centres throughout the kingdom. The Programme of the College, containing full particulars of the conditions of entrance, fees, and courses of instruction, may be had on application. *City and Guilds Central Technical College, Exhibition Road.*—Professor of Chemistry, H. E. Armstrong, Ph.D., F.R.S. The object of this Institution is to give to London a College for the higher technical education, in which advanced instruction shall be provided in those kinds of knowledge which bear upon the different branches of productive industry, whether Manufactures or Arts. The main purpose of the instruction given is to practically demonstrate the application of different branches of science to various manufacturing industries. In order that this instruction may be efficiently carried out, the Institution, in addition to the lecture theatres and class rooms, is fitted with laboratories, drawing offices, and workshops; and opportunities are afforded for the prosecution of original research, with the object of the more thorough training of the students, and for the elucidation of the theory of industrial processes. The courses of instruction are arranged to suit the requirements of—1. Persons who are training to become Technical Teachers; 2. Persons who are preparing to enter Engineers' or Architects' offices, or Manufacturing works; 3. Persons who desire to acquaint themselves with

the scientific principles underlying the particular branch of industry in which they are engaged. The Matriculation Examinations begin on Tuesday, September 21st, and the Winter Session opens on Tuesday, October 5th, *City and Guilds Technical College, Finsbury.*—Professor of Chemistry, Raphael Meldola, F.R.S. The operations of the Technical College, Finsbury, are divided into two distinct portions: Day Classes for those who are able to devote one, two, or three years to systematic technical education; Evening Classes for those who are engaged in industrial or commercial occupations in the daytime and who desire to receive supplementary instruction in the application of Science and of Art to the trades and manufactures in which they are concerned or employed. Each Professor is assisted by Demonstrators. Besides these there are Lecturers and Teachers in special subjects. An examination for the admission of Students will be held at the College on Tuesday, September 22nd. Session begins September 29th. *South London Technical Art School.*—Classes in Modelling, Design, Drawing and Painting, House Decoration.

CITY OF LONDON COLLEGE, White Street, Moorfields.—I. S. Scar, F.I.C., F.C.S., and Assistants. Courses of Saturday and Evening Lectures and Laboratory Practice in Chemistry and Physics, open to Students of both sexes. Day Commercial School. Session commences Sept. 27th.

BATTERSEA POLYTECHNIC.—Principal, Mr. S. G. Rawson, F.I.C. Inorganic, Organic, and Technological Chemistry, Mr. John Wilson, M.Sc. (Vit.), and Assistants. Session opens Sept. 27. Complete courses of instruction are given in Chemistry (Inorganic and Organic), together with Physics, Electricity, Engineering subjects, German, &c., for intending technological and works chemists. Certain of the Courses (Day and Evening) are recognised by the University of London in preparation for the B.Sc., for which examination (Pass and Honours) complete courses of instruction, under recognised teachers, are provided. Special Evening Courses in Technical Bacteriology, Paper Making, and Oils, Fats, Soap, and Candles.

BOROUGH POLYTECHNIC INSTITUTE, 103, Borough Road, S.E.—Chemistry Department under the Direction of C. D. Jones, M.A., D.Sc. Evening Lectures and Laboratory Work in Inorganic and Organic Chemistry. Special Lectures and Laboratory Courses in Electro-chemistry and Electro-chemical Analysis. Special Course of Lectures on Chemistry and Technology of the Essential Oils, by C. T. Bennett, B.Sc., A.I.C. Session opens Monday, Sept. 27.

BIRKBECK COLLEGE, Breams Buildings, Chancery Lane.—Chemistry Courses conducted by Dr. Alex. McKenzie prepare for various Examinations, the B.Sc. and M.B. Degrees of the London University, Conjoint Board, Pharmaceutical Examinations, Board of Education, &c. The Session will commence on Monday, Sept. 27, when Dr. H. A. Miers will give the Opening Address, at 7.30 p.m. The Day and Evening courses of study include Chemistry, Physics, Botany, Zoology, Geology, Mathematics, Latin, Greek, Modern Languages, Economics, Geography, Logic, and various branches of Law. Courses conducted by recognised teachers of the University provide for the Examinations of the University of London. The Calendar supplies detailed information respecting the Courses of Study, Examinations, &c.

NORTHERN POLYTECHNIC INSTITUTE, Holloway Road, N.—Principal, R. S. Clay, D.Sc.; Head of the Chemical Department, W. H. Mills, M.A., Sc.D.; Assistants, W. H. Watson, B.Sc., A.R.C.S.; Miss A. M. Bain, M.A., B.Sc.; and F. W. Linch, A.I.C. Instruction in theoretical and practical Inorganic and Organic Chemistry. Systematic Day and Evening Courses for the London University Degrees, Pass and Honours, also for the Board of Education examinations. The Session begins Sept. 20. Prospectus sent free on application to the Secretary.

NORTHAMPTON POLYTECHNIC INSTITUTE, St. John Street Road, E.C.—Principal, R. Mulineux Walmsley, D.Sc., &c.; Technical Chemistry, Mr. S. Field, A.R.C.S.;

Mr. A. H. Munday, F.C.S.; and Mr. G. Naylor. Day and Evening Classes in Electro-chemistry, Electroplating, Electro-metallurgy, Electrotyping, and Stereotyping. (For full details see Prospectus).

SOUTH WESTERN POLYTECHNIC, Chelsea, S.W.—Principal, Sidney Skinner, M.A. Head of the Chemical Department, J. B. Coleman, A.R.C.S., F.I.C. Day and Evening Courses in Theoretical and Practical Chemistry and several branches of Applied Chemistry including Metallurgy, Assaying, Photography, &c. Systematic Courses are held for the Matriculation, Inter. Sci., and B.Sc. Examinations (Pass and Honours) of the University of London. The Day Course in Chemistry is of three years' duration; it gives a thorough training to those who wish to become Consulting or Industrial Chemists. Prospectus of Day and Evening Classes may be obtained from the Secretary, *id.*, by post 4d.

EAST LONDON COLLEGE, Mile End Road, E.—Chemistry: Professor, J. T. Hewitt, M.A., D.Sc., Ph.D. Lectures and Practical Classes are conducted in the Day Technical College, the regular College Course being three years. The work of the first year corresponds with the requirements of the Int. Sci., Lond., that of the next two years with the degree examination, B.Sc. (Honours and Pass). Special attention is given to work for the Honours Examination and research. Evening Classes for London University Degrees are also held.

UNIVERSITY TUTORIAL COLLEGE, 32, Red Lion Square, Holborn, W.C.—This Institution contains large Laboratories for Chemistry, Physics, Geology, and other subjects. Classes are specialised for Examinations of London University, but students may take up work for any Examination. The special feature of the College is that work goes on all the year round, thus affording students residing in the Country an opportunity of doing practical work during their Vacations.

SIR JOHN CASS TECHNICAL INSTITUTE, Jewry Street, Aldgate.—Principal, Charles A. Keane, D.Sc., Ph.D., &c., assisted by H. Burrows, Ph.D., F.I.C., Arthur R. Ling, F.I.C., A. R. Smith, M.Sc., F.C.S., C. O. Bannister, A.R.S.M., Arthur Harden, D.Sc., J. S. S. Brame, and Wesley J. Lambert. The Session of the Sir John Cass Technical Institute will commence on Thursday, September 23rd. The Institute, which was founded by the Governors of Sir John Cass's Foundation, is specially devoted to technical training in experimental Science and in the Artistic Crafts. Graded curricula of study, extending over several years, are provided in the several departments of work, and in addition a number of special courses of instruction given by experts, so that there are full educational facilities in the subjects taught, both for youths and for those who have had no previous systematic training, and also for those holding responsible positions who desire to keep in touch with modern developments of the applications of science to industry. Amongst the special features of the syllabus for the new Session are courses of instruction on "Liquid, Gaseous, and Solid Fuel," arranged to meet the requirements of those engaged in chemical and engineering works or who are concerned with the use of fuel as a motive power; on the Fermentation Industries, including a special course on the Microbiology of the subject; on the various branches of Metallurgy, and on Scientific and Technical German. The aim of this last course is to provide for those engaged both in Pure and in Applied Science with an opportunity of acquiring a knowledge of scientific and technical terms employed in German with the view of enabling them to read German scientific and technical works and literature. Full details may be obtained on application, or by letter to the Principal.

EAST HAM TECHNICAL COLLEGE.—Principal, W. H. Barker, B.Sc. Chemistry, A. E. Dunstan, B.Sc. Evening Classes and Secondary School.

BLACKBURN MUNICIPAL TECHNICAL SCHOOL.—Chemistry: Mr. Robert H. Pickard, D.Sc. (Lond.), &c., assisted

by Messrs. Jos. Yates, M.Sc., F.I.C., W. O. Littlebury, B.Sc., F.I.C., Jos. Kenyon, B.Sc., A.I.C., and W. A. Jowitt. Session opens Monday, Sept. 20. Full details of the Classes are given in the "Students' Handbook," which may be had at the Institution (price 1d., by post 3d.).

LEEDS: CENTRAL TECHNICAL SCHOOL, Leeds Institute, Cookridge Street, Leeds.—Head Master, R. E. Barnett, B.Sc. (Lond.), A.R.C.S. Evening Classes are held in all subjects of Science and Technology, among which are:—Chemistry (Inorganic and Organic), Chemical Calculations and Principles of Analysis, by Mr. R. E. Barnett, B.Sc., A.R.C.S., Mr. J. B. Murray, Mr. A. McFarlane, and Mr. O. F. Kirby, M.A., B.Sc.; Metallurgy (Theoretical and Practical) and Iron and Steel Manufacture, by Mr. B. A. Burrell, F.I.C., F.C.S.; Gas Manufacture, by Mr. W. E. Pettigrew; Oils and Fats, by Mr. W. Dillon; Magnetism and Electricity, Practical Physics, &c., by Mr. J. E. Tindall, B.A., B.Sc.; Bread-making and Flour Confectionery, by Messrs. W. H. Quinn and J. C. Hesselgrave; Photography, by Mr. S. E. Bottomley. Fees: from 7s. 6d. per session. Group courses arranged for Students engaged in Chemical Industries. Special three evening Course for Pharmaceutical Students, covering the "Minor" syllabus in three years, by Messrs. J. H. Gough, Ph.C., F.C.S.; S. Parrish, B.Sc., A.R.C.S.; and N. Walker. Session commences Sept. 20th. See the Technical Handbook, 2d. (by post 5d.). Prospectuses of various Classes free on application to the Head Master, or to Mr. James Graham, Secretary for Education, Calverley Street, Leeds.

REDRUTH SCHOOL OF MINES, CORNWALL.—Principal, Henry C. Jenkins, Wh.Sc., A.R.S.M., Assoc. M.Inst.C.E., M.I.M. and M., &c., assisted by a staff of Mining Engineers and Mine Surveyors. Complete courses of Practical and Theoretical instruction are given in Inorganic Chemistry, Assaying, Mineralogy, Blowpipe Analysis, Mine Surveying, Geology, Principles of Mining, Ore Dressing, Mechanical Engineering, &c., for intending Assayers, Mineral Chemists, Mining Engineers, and Surveyors. Practical instruction in Mining given at the Basset Mines, Ltd. Syllabus on application.

MUNICIPAL SCHOOL OF TECHNOLOGY, Sackville Street, Manchester.—Laboratories and workshops for Mechanical, Electrical, Sanitary and Hydraulic Engineering, Textile industries, Photography, Collotype and Photo-mechanical processes, Letterpress and Lithographic industries, and industries within the scope of Architecture. The provision for the teaching of Chemistry, as might be expected in a district where the Chemical industries are important, is of an exceptionally complete character. It comprises laboratories for Metallurgy, Brewing, Bleaching, Dyeing and Printing, Paper-making, and Electro-chemistry. The Bleaching, Dyeing, Printing and Finishing, and the Paper-making industries are in addition extensively equipped in a separate building with machinery and appliances on an industrial scale. A Brew-house is also equipped on the low gravity principle, with a plant of four bushel capacity. The School is now established as the Faculty of Technology in the University of Manchester, and students of the School fulfilling the conditions can proceed to the Degrees of Bachelor and Master of Technical Science B.Sc. and M.Sc. Tech.). The Session commences Sept. 20.

WOLVERHAMPTON MUNICIPAL SCIENCE AND TECHNICAL SCHOOL.—Inorganic and Organic Chemistry, Mr. W. Whitehouse, F.C.S.; Physics, Messrs. W. Whitehouse and A. T. Harrison, B.Sc.; Botany, Mr. Sidney Phillips, Ph.C. Day Classes in Chemistry, and Evening Classes in Chemistry, Physics, Botany, French, &c. Special arrangements are made for the requirements of Pharmaceutical and Medical Students. Session commenced Monday, Sept. 13th. For other particulars and programme, apply Mr. G. F. Chell, Secretary.

MUNICIPAL TECHNICAL INSTITUTE, BELFAST.—Principal, F. C. Forth, A.R.C.S.I. Chemistry, Prof. J. Hawthorne, B.A., Ph.D., and Assistants. Day and Evening Courses. Session opened Sept. 13th.

THE CHEMICAL NEWS.

VOL C., No. 2600.

THE RELATION OF VOCAL QUALITY TO SOUND WAVES.*

By T. PROCTOR HALL, M.A., Ph.D., M.D.

AN apparatus for making enlarged tracings of sound waves from a cylindrical graphophone record, the magnification ranging from 150 to 2500 times, was described. In the sound waves two elements are distinguished, impulse and resonance, which are illustrated by waves from the cornet, violin, bugle, &c. Vocal waves are found in groups regularly repeated. Each group contains a single impulse from the vocal cords, together with one or more sets of resonance waves produced by vibrations of the air in the vocal tubes. Pitch is determined by the number of impulses per second—i.e., by the number of wave groups—and is not affected by the character of the waves within the groups. The vowel quality of vocal sounds is not perceptibly affected by the number or form of the resonance waves, but is dependent upon their periodicity. The rate of the resonance waves may be calculated from the length of the air tubes upward from the vocal cords. The calculation shows, for example, that the sounds *m*, *n*, *ng* all contain a resonance wave whose period is about 530. The mean rates found from measurements of the enlarged waves are for *m* 550, for *n* 535, for *ng* 580. The observed rate for the sound of *a* in the word "great" is 420, and for the sound of *a* in "mat" 770 waves per second. The investigation is continued.

ON CLARK AND WESTON STANDARD CELLS.*

By H. L. BRONSON, Ph.D., Assistant Professor of Physics,
and
A. N. SHAW, B.A., Demonstrator of Physics,
McGill University, Montreal.

THIS paper dealt mainly with the accuracy and reproducibility of Clark and Weston cells, and it is hoped that it may throw further light on the value of the cell as one of the two legal electrical standards.

The work has been very much facilitated by the courtesy of the Bureau of Standards at Washington, where one of the authors, at the suggestion of Dr. H. T. Barnes, spent some time in the summer vacation of 1908 in studying the construction of modern standard cells. At the invitation of Dr. P. A. Wolff we have been glad to actively co-operate with the Bureau in the work it has been doing along these lines.

I. The Reproducibility of the Cells when prepared according to the Specifications of Wolff and Waters.

The mean of fifteen Clark cells made in this way differed, a few weeks after their construction, from the mean of the reference cells of the Bureau of Standards by less than 14 microvolts. The average deviation of our cells from their own mean was not more than 13, while the maximum deviation was only 31 microvolts.

In the case of the Weston cells the figures were similar, but showed somewhat better agreement in every case; the difference between the mean of thirteen cells and the mean of the reference cells at the Bureau of Standards being in this case 4 microvolts, the average deviation of the cells from their own mean being 8, and the maximum deviation being 22.

* A Paper read before the British Association (Section A), Winnipeg Meeting, 1909.

Some of the Clark and Weston cells were made in Washington by one of the writers and subsequently transported to Montreal. A means of direct comparison with the values of the cells at the Bureau of Standards was thus obtained. This comparison has recently been checked by a second interchange of cells.

We have also had in our possession six Weston cells made at the National Physical Laboratory in London. One of these was damaged in transit; the mean of the other five differed from the mean of our other cells by only 5 microvolts.

II. The Effect of Introducing Slight Simplifications into the Preparation of Materials.

About twenty-five cells were constructed in order to examine the effects of slight simplifications in their preparation. It was found that the ingredient of main importance is the mercurous sulphate, which must always be prepared with great care. When unpurified mercurous sulphate was used in a cell, the average electromotive force was found to be from 300 to 500 microvolts higher than that of the normal cell. The purification of the zinc and cadmium salts is not so important, and as the processes are somewhat tedious, especially in the case of cadmium sulphate, it is interesting to see what accuracy may be obtained with various samples of chemically pure commercial sulphates. It was found that no Clark cell made with this modification differed by more than 50 microvolts from the mean of our normal cells, while no Weston cell differed by more than 100 microvolts. Such cells are therefore sufficiently accurate for all practical work.

The presence of basic oxide, oil, or small quantities of organic impurities was found to exert only a very small influence on the electromotive force.

III. The Relative Value of Cells set up according to the Board of Trade Specifications and those set up according to the Specifications of Wolff and Waters.

Ten Clark cells of the old "test-tube crystal" type were prepared from a number of different samples of chemically pure commercial materials, for the purpose of ascertaining how much they differed in voltage from those set up according to the modern specifications. The average electromotive force of these cells during the first seventy-five days, neglecting the first day, was 0.31 millivolt higher than the mean of our normal cells. The average deviation of these cells from their own mean was considerable, about 0.06 millivolt, which suggests that there might be a possible variation of three or four in the last figure of the mean for different batches of ten cells set up with different materials. It is therefore in good agreement with the value (0.00030 volt) given by Wolff and Waters.

IV. The Ratio of the Electromotive Force of the Weston Cell to that of the Clark.

The determination of this ratio, which had also been obtained at the Bureau of Standards, was made with the object of furnishing a further check on the reliability of the comparison between our cells and those of the Bureau, and to give added assurance that no errors had been introduced by transportation.

Five Clark cells were connected in series and placed in opposition to seven Westons similarly connected. The difference between the two sets was then measured on a Kelvin-Varley slide by the usual potentiometer method.

The ratio obtained was 0.716953, which differs from the ratio 0.716958, determined by Wolff and Waters, by only seven parts in a million. This difference, small as it is, is entirely accounted for by the small differences, as ascertained by direct comparison between our cells and those made at the Bureau of Standards.

Note.

There will also be given in the main paper an account of several cells made with mercurous sulphate prepared at the Bureau of Standards and dried with alcohol.

The results of a number of Weston cells of the normal type will be added to those mentioned in this abstract. Owing to large initial hysteresis their electromotive force had not, up to the time of writing, assumed their final value.

THE EFFECT OF TEMPERATURE VARIATIONS ON THE LUMINOUS DISCHARGE IN GASES FOR LOW PRESSURES.*

By ROBT. F. EARTHART.

THE apparatus used in this investigation consisted of a small glass bulb, in which two parallel electrodes were sealed. These electrodes were 5 mm. apart. Suitable tubes permitted the bulb to be evacuated, the pressures being measured with a McLeod gauge.

The bulb was contained in an electric furnace, which could also be used as a container for carbon dioxide snow when measurements for discharges occurring at low temperatures were taken.

Potentials required to produce a luminous discharge for pressures varying from 0.2 mm. to 5 mm. were made, and for temperatures varying from -78° C. to 325° C. The gases operated upon were air, hydrogen, and carbon dioxide.

Potentials required to maintain the luminous discharge under similar conditions were also measured. Families of curves showing the effects of temperature and pressure for potentials required both to produce and to maintain luminous discharge were given.

They indicate that Paschen's law holds approximately for the discharge in air until temperatures in the neighbourhood of 300° C. are attained. Here Paschen's law does not hold even approximately. The effect of temperature variation on the potential required to maintain the discharge is much less than for the production of the initial discharge.

THE MEASUREMENT OF ROTATORY DISPERSION.†

By T. MARTIN LOWRY, D.Sc., F.C.S.

MEASUREMENTS have been made with light of the following twenty-six wave-lengths:—

Li 6708; Na 5893; Ti 5351 (flame spectra).
Hg 5790 5769 5461 4359 (enclosed arc).
Cd 6438 5086 4800 4678; Zn 6364 4811 4722 4680.
Cu 5782 5700 5218 5153 5106 4705 4651 4587 4378.

A photographic method has also been devised by means of which measurements may be made throughout the transmitted spectrum, so far as this can be recorded on a photographic plate.

From the above list the seven wave-lengths shown in italic type have been selected for general use, the green mercury line, Hg 5461, being selected on account of its brilliance and purity as principal standard in place of the sodium doublet, 5890, 5896.

Measurements have been made of the optical and magnetic rotations produced by quartz and by a series of optically active alcohols, acids, and esters. In the case of quartz there is an absolute agreement between the two dispersions, but every optically active liquid that has been examined shows a divergence between the two series of values, the optical dispersion being usually, but not always, higher than the magnetic dispersion. It is possible that the identity of the optical and magnetic dispersions in crystals is an indication that the *magnetic* rotatory power

of liquids depends upon a spiral packing of the molecules of the same general character as that which produces the *optical* rotatory power of quartz, but the evidence at present available is not sufficient to justify a definite pronouncement.

THE ATOMIC WEIGHT OF IRIDIUM.* THE ANALYSIS OF POTASSIUM CHLOROIRIDATE.

By E. H. ARCHIBALD.

POTASSIUM chloroiridate has been prepared from two sources: 1. From 150 grms. of osmo-iridium ore obtained from Baker and Co., of Newark, N.J. 2. From metallic iridium obtained from Dr. Heraeus, of Hanau.

The potassium chloroiridate was analysed by weighing the dry salt, reducing it in hydrogen, and estimating the hydrochloric acid formed, the potassium chloride and the metallic iridium set free. The results show a value of 192.90 for the atomic weight of iridium.

THE ELECTRICAL CONDUCTIVITY OF SOLUTIONS OF IODINE AND OF PLATINUM TETRAIODIDE IN ETHYL ALCOHOL.*

By E. H. ARCHIBALD and W. A. PATRICK.

WHEN solutions of iodine in ethyl alcohol were examined as to their power of conducting the electric current, it was found that the conductivity increased rapidly with the time. This change appeared to be due to the progress of a reaction, the speed of which was greatly accelerated, at low temperatures, by the platinum black of the electrodes. At 25° the conductivity reaches a maximum in about twenty-five hours. The reaction goes on extremely slowly if platinum black is not present. As a result of this reaction the colour of the solution becomes lighter. The initial conductivity of the iodine-alcohol solution was very small. No evidence could be found of the formation of an addition compound between the iodine and alcohol at as low a temperature as -80° .

Platinum tetra-iodide forms good conducting solutions with alcohol. The molecular conductivity soon reaches a constant value.

MERCUROUS SULPHATE FOR STANDARD CELLS.*

By CHARLES J. J. FOX, B.Sc., Ph.D.

It is now well established that the chief cause of inconstancy in cadmium cells is usually due to irregularities in the mercurous sulphate. F. E. Smith has investigated this matter pretty exhaustively (*B.A. Reports*, Cambridge, 1904, p. 33), and has suggested four different methods for preparing reliable Hg_2SO_4 (South Africa, 1905, p. 98). The present author wishes to suggest a fifth method which he has used, and which for simplicity and reliability seems to be superior to any of them.

There is no difficulty in purchasing Hg_2SO_4 which is quite free from foreign metals. But these commercially pure preparations taken as they are are unsuitable for use in standard cells, because they have usually been precipitated from the nitrate solution in the cold, and are therefore not well crystallised; free nitrate and basic sulphate are also present. But if commercially pure Hg_2SO_4 be heated together with a little pure Hg and

* A Paper read before the British Association (Section A), Winnipeg Meeting, 1909.

† A Paper read before the British Association (Section B), Winnipeg Meeting, 1909.

* A Paper read before the British Association (Section B), Winnipeg Meeting, 1909.

dilute H_2SO_4 for a day or so at 120° to 150° in either a sealed tube (1 to 2 millimetre walled tubing) or bottle with wire-bound stopper, and occasionally agitated, a white crystalline preparation will be obtained even from a specimen of Hg_2SO_4 which is initially discoloured almost black. On opening the tube or bottle it will usually be noticed that the pressure has risen a little and that there is a trace of NO_2 formed; a little care should therefore be employed if there is more than a trace of nitrate in the original Hg_2SO_4 . But the Hg_2SO_4 obtained in this way is itself free from nitrate and especially if the H_2SO_4 be filtered off and renewed during the heating process; it is also, of course, quite free from basic salt. It is filtered off, ground up in a mortar with one or two successive quantities of diluted H_2SO_4 , and then with several quantities of saturated cadmium sulphate solution; it is filtered off in a Büchner funnel after each washing. In this way it is possible with very little trouble to prepare quite large quantities of very reliable well crystallised white Hg_2SO_4 in every suitable way for standard cells.

By heating with HCl and Hg , it is also a very convenient method of preparing crystalline calomel; but in this case the heating takes about twice as long owing to the small solubility of calomel compared with Hg_2SO_4 .

THE EVOLUTION OF WHEAT CULTURE IN NORTH AMERICA.*

By Prof. ALBERT PERRY BRIGHAM,
Secretary of the Association of American Geographers.

THE author spoke of the beginnings of wheat culture in the United States, the migration of the wheat centre from New York westward, and probable present centre of wheat for North America in view of recent extensions in Canada, and discussed the conditions by virtue of which wheat as a pioneer crop gives way to other and diversified agriculture; latitude range of wheat in North America as compared with other continents; extension of areal and latitude range through irrigation and through experimental modification and adaptation; the extent and significance of the migration of wheat growers from the United States into Canada; wheat extension in North America in relation to the evolution of transportation, both internal and trans-oceanic; the United States as an exporting country, and the possible overtaking of production by home demands; the future of Canadian wheat in the light of this possibility; the wheat problem of America in relation to the bread supply of the world.

A CONTRIBUTION TO OUR KNOWLEDGE OF THE NITROGEN PROBLEM UNDER DRY FARMING.†

By F. J. ALWAY, B.A., Ph.D.

FALLOWING, which in "dry farming" is necessary in order to accumulate water in the subsoil, facilitates the rapid loss of nitrogen, while the use of leguminous crops as green manures exhausts the moisture of the subsoil. The nitrogen problem will probably become acute much sooner in the central and southern portion of the semi-arid region than in Saskatchewan, as the original content of nitrogen is less. Six-inch samples of the heaviest types of soil, which are also those richest in nitrogen, were taken by the author from prairies in widely separated portions of the semi-arid region, viz., Indian Head, in Saskatchewan; North Platte, in Nebraska; Solana, in northern New Mexico; and Douglas, in south-eastern Arizona. The percentages of

nitrogen were 0.384, 0.175, 0.161, and 0.087 respectively, and of organic carbon 4.19, 2.06, 1.29, and 0.58.

The author reported the results of the determination of nitrogen, organic carbon, and soluble humus in over fifty samples of soil taken by him from different fields, plots, &c., of the Indian Head Experimental Farm, as well as from the adjacent prairie. The history of all the fields since the first prairie sod was turned is known. Continuous cropping with wheat, oats, and barley, with a fallow about every third year, has caused a loss of about one-third of the original content of nitrogen and carbon. Continuous bare cultivation for fifteen years has caused noticeably greater losses than cropping for the same length of time. Seeding down to grasses has checked the losses. In the case of a field of twenty-two rotation plots the average of the fifteen plots, on each of which during nine years a leguminous crop had been ploughed under every third year, was the same as that of the seven plots which had produced a cereal crop every year or had been fallowed every third year.

That nitrogen has not yet become a limiting factor in the yield of wheat at Indian Head is shown by the annual reports of the Indian Head farm. Applications of 100 and 200 lbs. of NaNO_3 have caused no increase in yield of wheat. The yield after leguminous crops ploughed under has been less than on fallows, the difference in yield seeming to depend upon the extent of growth and the lateness of ploughing of the legumes, and accordingly upon the amount of water removed from the soil by the legumes.

PROTEINS.*

THE RELATION BETWEEN COMPOSITION AND FOOD VALUE.

By E. FRANKLAND ARMSTRONG, Ph.D., D.Sc.

IT has been customary hitherto, when investigating the protein content of a food material, to determine the amount of nitrogen in it and multiply this by the factor 6.25. The quotient is spoken of as protein without any reference to its nature, although it has long been realised that proteins of different origin are not the same. The practice was perhaps justifiable so long as the chemistry of the proteins remained an almost unexplored field, but recent work, in particular that of Emil Fischer, Abderhalden, Osborne, and others, makes it possible to take up a more scientific position.

The proteins have been proved in the main to be built up of amino-acids, belonging both to the aliphatic and aromatic series, or derived from cycloids containing nitrogen, of oxyamino acids, and of diamino-acids. The careful analytical investigation of a large number of proteins has shown that these various structural units are present in very different proportions in the different proteins, and some of them may be altogether absent from a particular protein. Cereal proteins, for example, are characterised by a high percentage of glutamic acid, amounting to about 30 per cent in most cases, the legumes yield about 20 per cent, oil seeds about 17 per cent; meat proteins give only 8 to 11 per cent glutamic acid, but are characterised by containing much glycine.

The amino-acids are so very different from one another in their chemical structure that it must be supposed that they each fulfil somewhat different functions in building up the tissues of the body. It thus becomes important to see that each is supplied in the proper proportions required by the body. Further, the analytical results point to the impossibility of entirely replacing a diet composed of one kind of protein—for example, meat—by another diet composed, let us say, of nuts, since the two proteins, though made up of the same structural units, contain these in entirely different proportions.

* A Paper read before the British Association (Section E) Winnipeg Meeting, 1909.

† A Paper read before the British Association (Section K) Winnipeg Meeting, 1909.

* Read at the Joint Meeting of Sections B and I (Discussion on Food), British Association, Winnipeg Meeting, 1909.

Under the influence of the digestive enzymes, the proteins can be converted into the same amino-acids as are obtained when mineral acids are used to effect hydrolysis. If, however, the process of "building-down" be stopped before completion, compounds in which two or more amino-acids are joined together—the so-called polypeptides—can be isolated.

It remains now for the chemist and physiologist to solve such problems as the precise function and significance of each amino-acid in metabolism, how far they may replace one another or may be absent altogether without injurious effects; further, to what extent each is concerned in the maintenance of a particular tissue. Judging from the great variety of proteins consumed in a normal diet, it is obvious that everyone of the units at present known to us must be of importance, and a diet composed of one source of protein only or one which is too monotonous in character, even if derived from three or four different sources, is certainly to be condemned. Either will lead to the presence of an excess of particular amino-acids and of a deficiency of others perhaps equally important. All the evidence afforded by the chemical structure of the proteins goes, in fact, to show that they are not equivalent.

Probably the presence of most, if not all, of the various known amino-acids and other units of protein is necessary in a food if health is to be maintained. In this connection some experiments of Willcock and Hopkins may be cited (*Journ. Physiol.*, 1906, xxxv., 83), in which it was shown that young mice fed with zein as their only source of nitrogen soon died. When tryptophane, a unit which is absent in zein, was also administered, life was greatly prolonged; the addition of tyrosine—which, however, is a normal constituent of zein—had no such effect. Apparently the presence of some tryptophane is essential.

Some recent investigations of Abderhalden (*Zeit. Physiol. Chem.*, 1909, lviii., 334; lix., 170, 236), which possess considerable interest, may be quoted in illustration of the method of attack which will no doubt have to be followed in similar cases. As already indicated, it is a moot question whether the amino-acids can be changed in nature or in amount or synthesised from simpler fractions in the organism; to answer it a study has been made of the silk-worm, in which the problem is simplified by the fact that the worm takes no nourishment after it has begun to spin. The protein fibroin obtained from raw silk is characterised by yielding a large proportion of glycine and alanine, and a fair proportion of tyrosine when hydrolysed, and it is not without interest that both Italian and Canton silks are identical as regards the proportions of monoamino-acids they contain. Silkworms, when dried and hydrolysed in the same manner as fibroin, were found to contain large supplies of the very amino acids most abundant in the silk fibroins. (It does not, however, necessarily follow that the worm contains ready-formed silk protein in the liquid state). The worm gives rise to cocoon and moth. Continuing the investigation, the moths were likewise subjected to analysis. From them the yields of glycine, alanine, and tyrosine were very sensibly less, and the yields of the other amino-acids correspondingly higher than from the cocoons; in fact, the monoamino-acids obtained from the moths were equivalent in amount to those from the worms minus those from the cocoons. To complete the story, it obviously remains to investigate the nature and quantity of the monoamino-acids present in the proteins of the mulberry leaves which serve as food to the worms, and Professor Abderhalden's further results will be awaited with interest.

In comparing proteins it is not enough to establish the nature and amount of the structural units, but it is necessary further to study how the monoamino-acids are coupled together to di- and poly-peptides. Any pair of amino-acids can give rise to two isomeric dipeptides with different physiological properties. The dipeptide glycylalanine, for example, behaves quite differently towards digestive enzymes than does the isomeric alanylglycine. Presum-

ably a food containing the former would be less easily assimilated than one yielding the latter complex. This part of the subject is as yet in its infancy, but it may be expected to yield results of great significance.

To sum up, when discussing the value of foods, it is not enough to know merely the gross amount of nitrogen containing matter, but the nature and proportion of its constituent units must also be taken into account. The ideal diet should contain as much variety of protein as possible in order to provide sufficient of all the possible units of constructive metabolism.

THE SEVEN STYLES OF CRYSTAL ARCHITECTURE.*

By Dr. A. E. H. TUTTON, F.R.S.

THE proverbial importance of the number seven is once more illustrated in regard to the systems of symmetry exhibited by solid matter in its most perfectly organised form, the crystalline. For there are seven such systems or styles of architecture of crystals, just as there are seven distinct notes in the musical octave, and seven chemical elements in the octave or period of Newlands and Mendeleeff, the eighth or octaval note or element being but a repetition on a higher scale of the first.

A crystal appeals to us in two distinct ways, first compelling our admiration for its beautifully regular exterior shape, and next impressing us with the fact of its internal homogeneity, expressed in the cases of transparent crystals by its perfect limpidity, and the obvious similarity throughout its internal structure. As it is with human nature at its best, the external appearance is but the expression of the internal character.

The purpose of this discourse is not so much to dilate upon the seven geometrical systems of crystals, as to show how they are occasioned by differences in the internal structure, and to demonstrate this internal structure in an ocular manner, unfolding at the same time some interesting phases of recent investigation.

In order to remind ourselves of the seven crystal systems, a series of seven lantern slides will be exhibited, prepared from photographs of real small crystals, taken by the lecturer with the aid of the microscope and camera while in the act of formation on a microscope slide. To the Greeks, whose wonderfully perfect knowledge of geometry we are ever admiring, the cube was the emblem of perfection, for like the Holy City, lying "foursquare," described in the inimitable language of the book of Revelation, "The length and the breadth and the height of it are equal." Moreover, even when we have added that all the angles are right angles, these are not the only perfections of the cube, for they carry with them, when the internal structure is developed to its highest possibility, no less than twenty-two elements (thirteen axes and nine planes) of symmetry.

At the other extreme is the seventh, the triclinic system, in which the symmetry is at its minimum, neither planes nor axes of symmetry being developed, but merely parallelism of faces, sometimes described as symmetry about a centre, and in which there are no right angles and there is no equality among adjacent edges. Between these two extremes of maximum and minimum symmetry we have the five systems known as the hexagonal, tetragonal, trigonal, rhombic, and monoclinic, possessing respectively, 14, 10, 8, 6, and 2 elements of symmetry. (Photographs of real crystals belonging to all these seven respective systems were then thrown on the screen). All crystals do not possess the full symmetry of their systems, each system being subdivisible into classes possessing a definite number of the possible elements. Altogether there are thirty-two such classes, and their definite recognition we owe to the genius of von Lang and Story Maskelyne.

The characteristic property possessed in common by all

* A Discourse delivered before the British Association, Winnipeg Meeting, August 26, 1909.

crystals is that the exterior form consists of, and is defined by, truly plane faces, inclined, in accordance with one of the thirty-two classes of symmetry, at specific angles which are characteristic of the substance. This has only been proved to be an absolute fact within the last few years, although asserted by Haüy so long ago as the year 1783; for the numerous cases of so-called "isomorphous" salts, the first of which were discovered by Mitscherlich in the year 1820, were for long believed to be exceptions, and until the year 1890 no actual evidence one way or the other was forthcoming. But it was eventually shown that the crystals of the members of an isomorphous series did differ, both in their angles and in all their other crystallographic and physical properties, although in the cases of the angles the differences were very small. Moreover, the differences were shown to obey a simple but very interesting law, namely, that they were functions of the atomic weight of the chemical elements of the same family group whose interchange gives rise to the series. (A series of lantern-slides was next shown to illustrate this law).

All crystals possess one other obvious property, that of homogeneity, and we now know that it is the character of the homogeneous substance which determines the external form. There are no less than 230 different kinds of homogeneous structures, neither more nor less, the elucidation of which we owe to the independent recent labours of Schönbein, von Fedorow, and Barlow. And it is a significant fact that the whole of them fall naturally into the thirty-two classes of crystals, leaving no class unaccounted for. Of these 230 modes of regular repetition in space fourteen are the space-lattices long ago revealed to us by Bravais, and all recent investigation concurs in indicating two facts, first, that it is the space-lattice which determines the crystal system, and the second that it is the arrangement of the chemical molecules which is represented by the space-lattice. Each cell of the space-lattice corresponds to a molecule. The structure is certainly not solid throughout, however, part only being matter, and the rest ether-filled space, the relative proportions and the shape of the material portion being as yet unknown. We limit ourselves, therefore, to considering each molecule as a point, and we draw the lattice as a network of three systems of parallel lines, parallel to the directions of the three principal crystal edges, analogous, according to the system of symmetry, to those of the cube. The points of intersection we consider as those representing the molecules, inasmuch as any point within the limits of the cell may equally well be taken to represent the cell and the molecule, provided the choice is analogously made throughout the structure. Such a space-lattice, one of the most general, triclinic, form, is shown on the screen.

It has recently been found possible to determine the relative dimensions of these molecular cells, the distances of separation of the points of the space-lattice, in those cases where we know that the structure is similar, as in isomorphous salts; and the interesting discovery has been made that the "molecular distance ratios," as these space-dimensions are called, are functions of the atomic weights of the interchangeable members of the family of chemical elements constituting the series, just as the crystal angles have been shown to be.

We are now able, moreover, to take yet one further step, for the chemical molecules are composed of atoms, and it has been indubitably shown that the atoms occupy definite positions in the crystal. For when we replace, say, the alkali metal in a sulphate or selenate, by another, we observe a marked alteration in the crystal angles and the molecular distance ratio along a particular direction, this direction being the same whichever metals of the group are interchanged; whereas if we replace the sulphur by selenium, a similar kind of alteration occurs, but along a totally different direction. Now we know that the atoms are arranged in the chemical molecule in what is known to chemists as their stereometric arrangement, depending on the maximum satisfaction of their chemical affinities. Hence this important experimental fact of the occupation

by the atoms of definite positions in the crystal proves, firstly, the homogeneous similarity of arrangement of the molecules, and, secondly, explains why we have classes or sub-divisions within the systems. For it is the arrangement of the atoms within the molecule which causes the variations of the degree of symmetry, within the limits prescribed by the system and space-lattice; in other words, which determines the class.

Now obviously any one of the atoms in the molecule may be chosen to represent the latter, and the points thus chosen analogously throughout the structure will constitute the molecular space-lattice. Hence the whole structure may be considered as made up of as many interpenetrating similar space-lattices as there are atoms in the molecule. The crystal structure will thus be dependent on two factors, the space-lattice and the scheme of interpenetration of the space-lattices, the former dominating the style of architecture, the crystal system, and the latter the vagaries of the style, the crystal class. Sohncke has shown that there are sixty-five such vagaries possible, which he terms regular point systems, and these coincide with sixty-five of the 230 possible modes of partitioning space.

These are the broad simple facts, now proved up to the hilt, which explain the majority of crystal structures, all, in fact, but a very few, of the more complicated classes of the thirty-two. For the remaining 165 ways of appropriating space all fall into a very small number of crystal classes. They are of very great interest, however, and involve an entirely new principle, that of "reflective" or "mirror-image" symmetry, enantiomorphism as it is technically termed, and include those crystals which possess the remarkable property of rotating the plane of polarised light. These are the cases whose geometrical possibility has been accounted for by the simultaneously independent work of Schönbein, von Fedorow, and Barlow, and to which we were experimentally introduced by the discovery of the right- and left-handed varieties of tartaric acid by Pasteur. The latter has since been followed by the revelation of many similar cases of two forms of the same chemical substance, related crystallographically and structurally like a right-hand to a left-hand glove, and optically differing by the direction in which they rotate a beam of plane polarised light.

With their discovery and explanation the elucidation of the seven styles of crystal architecture and their thirty-two sub-divisions becomes *un fait accompli*, and although many difficult problems still confront the crystallographer, problems of vast importance to chemistry, the groundwork is now securely laid, the memorable achievement of the last twenty years. The results, moreover, are in entire accordance with the now well-proved fact that the chemical atom is composed of electronic-corpuscles. For the definite orientation of the atom and its sphere of influence within the molecule and the crystal is thereby accounted for, the motion in the solid state so frequently hitherto attributed to the atom being a myth, such motion relating, in fact, to the corpuscles within the atom.

The rest of this discourse will now be devoted to experimentally demonstrating, with the aid of a projection Nicol-prism polariscope of original construction, firstly, the optical behaviour of the simpler kinds of crystal structure, and, secondly, that of the interesting cases of mirror-image symmetry. Quartz in particular will afford us not only some magnificent phenomena by reason of its right- or left-handed structure, but also a most instructive example, in its repeatedly twinned and all-but-molecularly alternating variety of amethyst, of the phenomenon of "pseudoracemism." For it is the display of this phenomenon which often renders a crystalline inactive substance so difficult to distinguish from a truly "racemic" substance, which, as in the case of racemic acid itself, the optically inactive variety of tartaric acid, is a truly molecular compound of the right- and left-handed active varieties, the optical activity being neutralised and destroyed by the act of combination.

DETERMINATION OF TANTALUM AND NIOBIUM, AND SEPARATION FROM SILICA IN MINERALS, STEEL, AND ALLOYS.

By Dr. W. E. von JOHN.

For determination of tantalum and niobium in minerals these are fused with potassium bisulphate, the cooled melt is boiled with water. The insoluble matter is washed well with hot water, then several times with hot yellow ammonium sulphide, then again with hot water and dilute sulphuric acid, and finally with hot water. The residue consists of silica, tantalum and niobic acid; ignite and weigh. The separation of tantalum and niobium from silicon is based on the fact that potassium hexatantalate and niobate are soluble in water as well as in potassium hydrate, but the corresponding sodium salt only in water. (The method given by C. G. Taylor, "Dissertation," Columbia University, U.S.A., does not seem to be always satisfactory, as I have found that on evaporation of hydrofluoric acid by strong heating some of the tantalum and niobium is vaporised, TaF_5 and NbF_5 ; this method gives only good results by most careful evaporation at lowest possible temperatures, and careful regulation of the same). Fuse the ignited residue (SiO_2 , Ta_2O_5 , and Nb_2O_5) with sodium hydrate in a silver crucible; dissolve the cooled melt in cold dilute sodium hydrate solution, and filter through a Gooch crucible; wash several times with dilute sodium hydrate. This first filtrate contains the sodium



silicate. Wash the filter which still contains the sodium tantalate and niobate with lukewarm water several times until the filtrate does not give a precipitate by addition of dilute sulphuric acid. I would recommend the use of a test-tube inside the filter-bottle; this allows a most accurate collection of the filtrate.

This second filtrate will not be quite clear, due to the presence of some sodium hydrate, and therefore a formation of microscopic crystals of sodium hexatantalate and niobate in the solution. Precipitate the tantalum and niobium by addition of dilute sulphuric acid to the latter solution, and boil for a few minutes; filter, ignite, and weigh. The difference gives the SiO_2 and $Ta_2O_5 + Nb_2O_5$. Fuse again with potassium hydrate; dissolve the melt in water, and precipitate again with dilute sulphuric acid, boiling to obtain complete precipitation. Filter off, and dissolve the precipitate in hydrofluoric acid, add some potassium fluoride, and boil for a few minutes; dilute the solution with water and repeat boiling. All the tantalum is separated out as a practically insoluble potassium oxyfluoride ($K_4Ta_4O_5F_{14}$). The most soluble potassium niobium oxyfluoride is left in solution. (This method allows us to detect traces of tantalum in presence of niobium). Wash the residue with cold water until no reddish precipitate is obtained with tincture of galls, add pure concentrated sulphuric acid, and heat gently until all hydrofluoric acid is removed. Hereby Ta_2O_5 and $KHSO_4$ are formed; filter, and remove the latter by repeated washing with water; ignite and weigh.

In the case of estimation of tantalum in steel, dissolve the turnings in hydrochloric acid, evaporate to dryness, dissolve again in dilute sulphuric acid. The residue, which consists of silica, carbonaceous matter, and tantalum, is

filtered off, ignited, weighed, and fused with sodium hydrate and treated as described above.

In case of estimation of tantalum in ferro-tantalum or alloys with up to about 45 per cent tantalum, these could be treated in the same manner as steel. Above 45 per cent tantalum the fine powdered ferro-tantalum should at first be ignited and then treated as in case of steel, or, in presence of tin, as described for minerals.

These methods gave very satisfactory results, are most rapid, and could especially be recommended for commercial analysis.

Elswick Works, Newcastle-on-Tyne.

SILVER CYANAMIDE.

By H. RUSSELL ELLIS, B.Sc.

In order to estimate the cyanamide and hence the nitrogen in sodium cyanamide and in nitrolim, the following method was put forward by R. Perotti (*Journ. Chem. Soc.*, 1905, Abstr. ii., 870):—

The cyanamide was precipitated from a distinctly but not too strongly ammoniacal solution by means of an excess of standard $AgNO_3$ solution. The solution was warmed gently in order to coagulate the yellow precipitate of silver cyanamide; the precipitate was filtered off and well washed, and the silver remaining in the solution estimated by means of standard ammonium thiocyanate solution. From this the amount of Ag in the precipitate was determined, and assuming that silver cyanamide possessed the formula Ag_2CN_2 the percentage of cyanamide or N in the original substance could be found.

This method gives good results for pure substances, but with commercial sodium cyanamide, with nitrolim, and with soils containing nitrolim, the results were influenced very considerably by various impurities.

In Perotti's method, any sulphide, cyanide, or chloride may be thrown down with the cyanamide, and consequently the amount of $AgNO_3$ used will not be due to cyanamide alone, the result therefore being too high; again, some of the silver salts may dissolve in the ammonia used, and may interfere with the estimation of the excess of Ag.

To overcome these errors the following method was put forward, and has been found to yield very concordant results:—

I. Estimation of Cyanamide and Cyanide in Sodium Cyanamide.

A solution of the substance of about N/10 strength is prepared, and 20 cc. added to about 40 cc. of N/10 $AgNO_3$ and 10 cc. N HNO_3 , a precipitate of $AgCN$ obtained. This is filtered off and well washed, the filtrate and washings run into 20 cc. N NH_4OH , and the solution warmed. A precipitate of Ag_2CN_2 is obtained, which is filtered off and well washed.

The $AgCN$ precipitate is washed into a flask containing HNO_3 , and boiled until all the cyanide is dissolved, and the Ag then estimated by N/50 NH_4CNS . To estimate the Ag_2CN_2 dilute HNO_3 (1 HNO_3 , 5 water) is poured through the filter-paper, the residue well washed, and the silver estimated by NH_4CNS . From the Ag in each case the percentage of cyanide and cyanamide can be determined.

II. Estimation of Nitrolim.

1 to 2 grms. of very finely powdered substance is shaken with water and filtered into a 500 cc. flask, and well washed until a drop gives no precipitate with ammoniacal $AgNO_3$ solution.

20 cc. of this solution are added to excess of $AgNO_3$ solution (about 30 cc. N/10 solution) and 20 cc. N NH_4OH , the precipitate filtered, and thoroughly washed with warm water. Dilute HNO_3 (1 acid to 5 water) is poured over the residue, and well washed to remove all Ag_2CN_2 , and the Ag in the filtrate and washings then estimated by

standard NH_4CNS ; any Ag_2S or AgCl remains on the filter-paper. Any fluoride present in the cyanamide will not dissolve in water, or if any dissolves it is not precipitated.

This method of estimation has been used by the authors in studying the rate of decomposition of cyanamide under various conditions, especially in soils which contain nitrogen, chlorides, and sulphides, and is both rapid, convenient, and accurate (see paper by Weston and Ellis, read before Seventh International Congress of Applied Chemistry, 1909).

In the various methods employed it was assumed that silver cyanamide possessed the formula Ag_2CN_2 ; in order to make certain about this an investigation was undertaken.

Preparation of Silver Cyanamide.

About 30 grms. of nitrolim were dissolved in cold water and filtered; to this solution was added 20 cc. of strong ammonia and then excess of silver nitrate; the solution with the precipitate was warmed, filtered, and the yellow silver cyanamide thoroughly washed on a Buchner funnel on a filter-pump; it was then dissolved by pouring cold dilute HNO_3 over the filter-paper. Most of the Ag_2S , AgCl , and AgCN which had been precipitated along with the silver cyanamide remained undissolved by the HNO_3 ; the cyanamide was at once re-precipitated by excess of ammonia, and the process repeated five times until no residue remained which was insoluble in cold dilute HNO_3 . The silver cyanamide was left in a desiccator for two months over strong H_2SO_4 , and when required for use was perfectly dry and was in the form of a soft amorphous yellow powder.

Effect of Heat on the Powder.

When the yellow powder is heated rapidly in a crucible it explodes violently and is entirely ejected; on, however, carefully heating the explosion is quieter, and only a portion is thrown out; the residue consists of silver, and is at first slightly dark, but on heating strongly becomes white. When the heating is effected in a test-tube a very distinct smell of cyanogen is produced and a dark deposit is formed on the sides of the test-tube consisting probably of para cyanogen.

Estimation of Silver in the Silver Cyanamide.

1. By heating and weighing the silver left. The weighed substance, about 0.5 gm., was heated very gently in a weighed hard glass test-tube, closed at the top with a plug of previously ignited asbestos wool. After the explosion the test-tube and its contents was strongly heated for fifteen minutes and weighed after cooling. From this 84.78 and 84.18 per cent of Ag found; theory for Ag_2CN_2 is 84.36, theory for AgHCN_2 is 72.5.

2. By dissolving a weighed amount of the substance in HNO_3 and estimating the silver with standard NH_4CNS , using ferric sulphate as indicator. Two estimations gave 83.3 per cent of Ag; these are low, but considered with the above are sufficiently near to decide between the two formulæ Ag_2CN_2 and AgHCN_2 .

Estimation of Gases Evolved during Explosion.

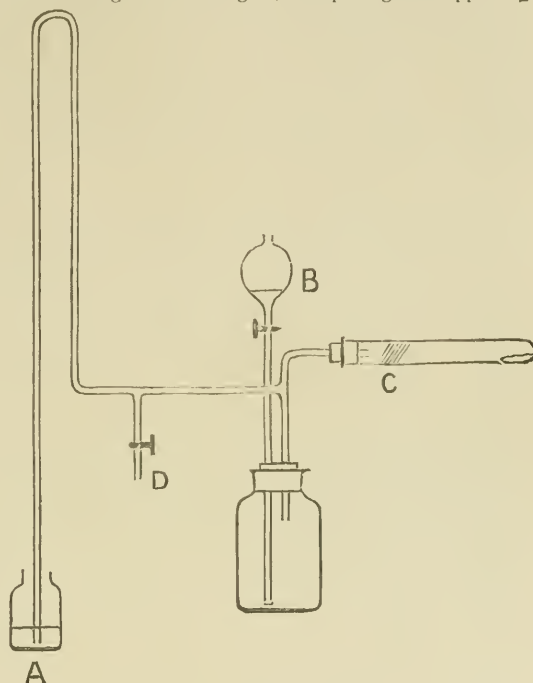
A weighed amount of the powder was placed in the hard glass test-tube, which in some experiments was also weighed, the apparatus fixed up as shown and exhausted by the Töpler pump, and tested for leaks. After exhausting no change was noticed in the manometer during two hours; the hard glass test tube was then gently warmed until the explosion took place, and then strongly heated for twenty minutes.

The explosion was quiet, and no gas was blown out through the manometer. The whole of the substance was changed and thrown up the tube, none however passing through the asbestos; a slight dark deposit was formed on the sides of the test-tube.

Measurements of the manometer and of the total volume of air required to fill the apparatus gave the volume of gas in the apparatus at any time.

After the heating the apparatus was cooled, and when the mercury level in the manometer was constant the reading was made.

A known volume of 20 per cent KOH solution was run in through the tap funnel, and after standing some two hours until the mercury level was again constant another reading was taken. The gas dissolved was cyanogen, and the residual gas was nitrogen; on opening the apparatus



A, Mercury manometer. B, 10 cc. KOH solution. C, Asbestos wool. D, To Töpler pump.

no smell of cyanogen could be observed. From the data obtained, and allowing for the change in pressure due to adding the KOH, the volumes of gas at N.T.P. were obtained. If the decomposition occurs in accordance with the equation $2\text{Ag}_2\text{CN}_2 = 4\text{Ag} + \text{C}_2\text{N}_2 + \text{N}_2$, 1 gm. should yield—

43.64 cc. of N and 43.64 cc. $(\text{CN})_2$ at N.T.P.

Experiment gave—

41.60 cc. of N and 31.79 cc. $(\text{CN})_2$ at N.T.P.

The decomposition is evidently closely represented by the equation given; the lowness of the cyanogen is due to the formation of solid para cyanogen. In each experiment carried out a similar result was obtained.

About 96 per cent of the silver cyanamide was converted into Ag after the first explosion, and the remainder changed after heating.

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Weights and Measures Regulations.—Chemists and druggists are having their attention again directed to the Weights and Measures Regulations, as a new Clause which seriously affects them comes into operation on October 1st. It is the degree of sensitiveness the scales must possess which requires their careful watching, as their scales must now be either Class A or Class B. When it is pointed out that no greater error either in excess or deficiency is allowed than 1 grain with a scale having a weighing capacity of 1 lb., it can easily be understood that the greatest care is necessary in order to satisfy these new requirements. We might add that the Inspectors of Weights are always ready to give any information respecting these regulations.

A NEW METHOD OF ISOLATING TERBIA.

By G. URBAIN.

THE terbia by means of which I was enabled to give a complete and exact description of Mosander's terbiuim was obtained by fractionating a mixture of gadolinium and terbiuim with dilute ammonia (*Comptes Rendus*, cxli., 521). In these conditions the terbia, which is a weaker base than gadolinia, is precipitated first.

This method is very tedious because of the many filtrations, washings, and concentrations it involves. I arrived at the same result with very much less trouble, though only after a longer time, by a crystallisation method, which in principle resembles that by which Lacombe and I completely separated europium from samarium (*Comptes Rendus*, cxxxvii., 792).

I have previously shown (*Journ. Chim. Phys.*, 1906, pp. 31–66) that bismuth comes between samarium and europium as regards the solubility of its salts which are isomorphous with the corresponding salts of the rare earths. Moreover, the order in which the rare earths are separated from one another by difference of solubility is independent of the nature of the salts. This order is as follows:—Lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbiuim, dysprosium, holmium, yttrium, erbium, thulium, neoytterbiuim, lutecium.

But in certain cases the series doubles back upon itself. This is the case with the simple nitrates with five molecules of water for instance, of which the gadolinium salt is the least soluble of all. These nitrates are grouped in such a way that neodymium occurs with erbium (E. Demarçay, *Comptes Rendus*, cxxx., 1021), and cerium and lanthanum with neoytterbiuim and lutecium in the most soluble fractions.

This doubling back of the series recalls the phenomenon of abnormal dispersion. I thought that it would be possible to take advantage of it to separate some of the rare earths from one another by using bismuth as the separating element.

Preliminary experiments (*Journ. Chim. Phys.*, 1906, pp. 105–122) performed with mixtures in which the terms preceding gadolinium had been eliminated previously, showed that bismuth nitrate, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, is more soluble in nitric acid than gadolinium nitrate, $\text{Gd}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, and less soluble than dysprosium nitrate, $\text{Dy}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$. On a first analysis, terbiuim nitrate appeared to have the same solubility as bismuth nitrate. Lengthy experiments have recently shown that bismuth nitrate is a little less soluble than terbiuim nitrate, so that by adding large quantities of bismuth nitrate to the mixture, and subjecting the whole to systematic crystallisation for a sufficiently long time, it would be possible to separate completely the gadolinium from the terbiuim.

As a matter of fact, I have not quite obtained such a remarkable result. When I thought I had reached it, the purest bismuth fractions still contained about four thousandths of terbiuim. In the following fractions the proportion of terbiuim slowly increased.

The examination of the arc spectra showed me that this new method, which is very different from that which I had first employed for the isolation of terbiuim, gave exactly the same earth, and that therefore there is no reason for suspecting the homogeneity of this element. These observations confirm the conclusions which Jantsch and I (*Comptes Rendus*, cxlvi., 127) drew from the determination of the available oxygen in terbiuim peroxide, Tb_4O_7 .

With the three fractions in which the proportion of terbiuim was large enough to enable magnetic measurements to be made, I performed new determinations of the coefficient of magnetisation of the sesquioxide of terbiuim, the values of which practically agree with those which Jantsch and I have already obtained (*Comptes Rendus*, cxlvii., Dec. 28, 1908). These new values agree particularly well:—

Fractions.	$\times 10^6$.
I I	242.7
I 2	242.5
I 3	243.2

I may mention that the method just described ensures the complete separation of the terbiuim from the dysprosium, because it enables the intermediate mixtures to be reduced to a minimum—the excess of bismuth sending the dysprosium towards the end of the fractionations, and retaining the small quantities of terbiuim which it is so difficult to eliminate by other methods.

With regard to some of the results given in this article, I must mention that Stephan Meyer (*Sitz. Ber. Wien. Akad.*, Jan. 23, 1902), having obtained some samarium and europium from Demarçay himself, corrected his first conclusions, and proved that the paramagnetism of the rare earths shows two maxima, one in the ceric series, the other in the yttric series. I am pleased to admit the priority of Stephan Meyer, whose second article I had not seen.—*Comptes Rendus*, cxlix., 37.

THE WORLD OF LIFE: AS VISUALISED AND INTERPRETED BY DARWINISM.*

By ALFRED RUSSEL WALLACE, O.M., D.C.L., LL.D., F.R.S.

THE lecturer began by stating that, although the theory of Darwinism is one of the most simple of comprehension in the whole range of science, there is none that is so widely and persistently misunderstood. This is the more remarkable, on account of its being founded upon common and universally admitted facts of nature, more or less familiar to all who take any interest in living things; and this misunderstanding is not confined to the ignorant or unscientific, but prevails among the educated classes, and is even found among eminent students and professors of various departments of biology.

Darwinism is almost entirely based upon those external facts of nature, the close observation and description of which constituted the old fashioned "Naturalists," and it is the specialisation in modern science that has led to the misunderstanding referred to. Those who have devoted years to the almost exclusive study of anatomy, physiology, or embryology, and that equally large class who make the lower forms of life (mostly aquatic) the subject of microscopical investigation, are naturally disposed to think that a theory which can dispense with all their work (though often strikingly supported by it) cannot be so important and far-reaching as it is found to be.

Numbers, Variety, and Intermingling of Life-forms.

Coming to the first great group of facts upon which Darwinism rests, the lecturer called attention to the great number of distinct species both of vegetable and animal life found even in our own very limited and rather impoverished islands, as compared with more extensive areas. Great Britain possessed somewhat less than 2000 species of flowering plants, while many equal areas on the Continent of Europe have twice the number. The whole of Europe contains 9000 species, and the World 136,000 species already described; but the total number, if the whole earth were as well known as Europe, would be almost certainly more than double that number, or about a quarter of a million species. The following table showing how much more crowded are the species in small than in large areas was exhibited on the wall. It affords an excellent illustration of the fact of the great intermingling of species, so that large numbers are able to live in close contact with other, usually very distinct, species.

Abstract of a Discourse delivered before the Royal Institution, January 22, 1909.

Numbers of Flowering Plants.

	Square miles.	Species.
The County of Surrey ..	760	840
A portion containing ..	60	660
" " ..	10	600
" " ..	1	400

(Other tables illustrating similar facts in other parts of the world were prepared, but not exhibited, as being likely to distract attention from the lecture itself).

The above figures were given by the late Mr. H. C. Watson, one of our most eminent British botanists, and as he lived most of his life in the county, they are probably the results of his personal observation, and are therefore quite trustworthy.

Continuing the above enquiry to still smaller areas, one perch equalling 1/160 acre, or less than the 1/100000 of a square mile, has been found to have about 40 distinct species, while on a patch 4 ft. by 3 ft. in Kent (or about 1/25,000,000 of a square mile) Mr. Darwin found twenty species.

The same law of increase of numbers in proportion to areas applies to the animal world, if we count all the species that visit a garden or field during the year, though those that can continuously live there are not perhaps so numerous in very small areas.

The Increase of Plants and Animals.

The powers of increase of plants and animals were next discussed, and were shown to be enormously great. An oak tree may produce some millions of acorns in a good year, but only one of these becomes a tree in several hundred years, to replace the parent. Kerner states that a common weed, *Sisymbrium Sophia*, produces about three-quarters of a million of seeds; and if all these grew and multiplied for three years, the plants produced would cover the whole land surface of the globe.

Equally striking is the possible increase in the animal world. Darwin calculated that the slowest breeding of all animals, the elephant, would in 750 years, from a single pair, produce nineteen millions. Rabbits, which have several litters a year, would produce a million from a single pair, in four or five years, as they have probably done in Australia, where they have become a national calamity. As illustrative of this part of the subject, the lecturer referred at some length to the cases of the bison and the passenger pigeon in North America, and the lemmings of Scandinavia. In the insect tribes still more rapid powers of increase exist. The common flesh-fly goes through its complete transformations from egg to perfect insect in two weeks; and Linnæus estimated that three of these flies could eat up a dead horse as quickly as a lion.

It is these enormous powers of rapid increase that have ensured the continuance of the various types of existing life from the earliest geological ages in unbroken succession; while it has also been an important factor in the production of new forms which have successively occupied every vacant station with specially adapted species.

Inheritance and Variation.

The vitally important facts of inheritance with variation was next discussed, and their exact nature and universal application pointed out. The laws of the frequency and the amount of variations, and their occurrence in all the various parts and external organs of the higher animals, was illustrated by a series of diagrams. These showed the actual facts of variation in adult animals of the same sex obtained at the same time and place, which had been carefully measured in numbers varying from twenty to several thousand individuals.

The general result deduced from hundreds of such measurements and comparisons was, that the individuals of all species varied around a mean value—that the numbers became less and less as we receded from that mean, and that the limit of variation in each direction was soon

reached. Thus, when the heights of 2600 men, taken at random, were measured, those about 5 ft. 8 in. in height were found to be far the most numerous. About half the total number had heights between 5 ft. 6 in. and 5 ft. 10 in., while only ten reached 6 ft. 6 in., or were so little as 4 ft. 10 in., and at 6 ft. 8 in. and 4 ft. 8 in. there were only one of each.

The diagrams from the measurements of various species of birds and mammals were shown to agree exactly in general character; and the further fact was exhibited by all of them, that the parts and organs varied more or less independently, so that the wings, tails, toes, or bills of birds were often very long, while the body, or some other part was very short, a point of extreme importance, as supplying ample materials for adaptation through natural selection.

The Law of Natural Selection.

The next subject discussed was the nature and mode of action of natural selection. It was pointed out that since the glacial epoch, no decided change of species had occurred. This showed us that the adaptation of every existing species to its environment, was not only special but general. The seasons changed from year to year, but the extremes of change only occurred at long intervals, perhaps of many centuries, with lesser but still very considerable variations twice or thrice in a century. It was by the action of these seasons of extreme severity at long intervals, whether of arctic winters or summer droughts, that the very existence of species was endangered; and it was at such times that the enormous population of most species and their wide range over whole continents, always secured the preservation of considerable numbers of the best adapted in the most favoured localities. Then the rapidity of multiplication came into play, so that in two or three years the population of each species became as great as ever; while, as all the least favourable variations had been destroyed, the species as a whole had become better adapted to its environment than before the almost catastrophic destruction of such a large proportion of them.

It is the fact of the adaptation of almost all existing species to a continually fluctuating environment—fluctuating between periodical extremes of great severity—that has produced an amount of adaptation that in ordinary seasons is superfluously complete. This is shown by the well-known fact that large numbers of adult animals that have not only reached maturity, but have also produced offspring and successfully reared them, continue to live and breed for many years in succession, although varying considerably from the mean, while almost the whole of the inexperienced young fall victims to the various causes of destruction that surround them.

The Nature of Adaptation.

The next subject discussed was the complex nature of adaptations in many cases, and probably in all; a subject of great extent and difficulty. The lecturer directed special attention to the relations between the superabundance of vegetation in spring and summer, the enormous, but to us mostly invisible, hosts of the insect tribes which devour this vegetation, and the great multitudes of our smaller birds whose young are fed almost exclusively on these insects. Without these hosts of insects the birds would soon become extinct; while without the birds, the insects would increase so enormously as to destroy a considerable amount of vegetable life, which would, in its turn, lead to the destruction of much of the insect and even of the highest animal groups, leaving the world greatly impoverished in its forms of life.

The vast numbers of insects required daily and hourly to feed each brood of young birds was next referred to, and the wonderful adaptation of each kind of parent bird which enables it to discover and to capture a sufficient quantity immediately around its nest, in competition with many others engaged in the same task in every copse and garden, was next pointed out. The facts were shown to involve

specialities of structure, agility of motions, and acuteness of the senses, which could only have been attained by the preservation of each successive slight variation of a beneficial character throughout geological time; while the emotions of parental love must also have been continuously increased, this being the great motive power of the strenuous activity exhibited by these charming little creatures.

Lord Salisbury on Natural Selection.

As illustrating the strange and almost incredible misconceptions prevailing as to the mode of action of natural selection, the lecturer quoted the following passage from the late Lord Salisbury's presidential address to the British Association at Oxford in 1894. After describing how the diverse races of domestic animals have been produced by artificial selection, Lord Salisbury continued thus:—

"But in natural selection who is to supply the breeder's place? Unless the crossing is properly arranged the new breed will never come into being. What is to secure that the two individuals of opposite sexes in the primeval forest, who have been both accidentally blessed with the same advantageous variation, shall meet, and transmit by inheritance that variation to their successors? Unless this step is made good the modification will never get a start; and yet there is nothing to ensure that step but pure chance. The law of chance takes the place of the cattle-breeder or the pigeon-fancier. The biologists do well to ask for an immeasurable expanse of time, if the occasional meetings of advantageously varied couples, from age to age, are to provide the pedigree of modifications which unite us to our ancestors, the jelly-fish."

Here we have the extraordinary misconception presented to a scientific audience as actual fact, that advantageous variations occur singly, at long intervals, and remote from each other; each statement being, as is well known, the absolute reverse of what is really the case. It totally ignores the fact, that every abundant species consists of tens or hundreds of millions of individuals, and that as regards any faculty or quality whatever, this vast host may be divided into two portions—the *less* and the *more* adapted—not very unequal in amount. It follows that at any given time, in any given country, the advantageous variations always present are not to be counted by ones and twos, as stated by Lord Salisbury, but by scores of millions; and not in individuals widely apart from each other, but constituting in every locality or country somewhere about one half of the whole population of the species.

The facts of nature being what they are, it is impossible to imagine any slow change of environment to which the more populous species would not become automatically adjusted under the laws of multiplication, variation, and survival of the fittest. Almost every objection that has been made to Darwinism assumes conditions of nature very unlike those which actually exist, and which must, under the same general laws of life, always have existed.

Protective Colour and Mimicry.

The phenomena of protective coloration and mimicry were very briefly alluded to, both because they are comparatively well known and had formed the subject of previous lectures; while they are very easily explained on the general principles now set forth. The explanation is the more easy and complete, because of all the characters of living organisms, colour is that which varies most, is most distinctive of the different species, and is almost universally utilised for concealment, for warning, or for recognition. And further, its useful results are clear and unmistakable, and have never been attempted to be accounted for in detail by any other theory than that of the continuous selection of beneficial variations.

The Dispersal of Seeds.

The subject of the dispersal of seeds through the agency of the wind, or of carriage by birds or mammals in a variety of ways, and often by most curious and varied arrange-

ments, of hooks, spines, or sticky exudations almost infinitely varied in the different species, was also briefly treated, since they are all readily explicable by the laws of variation and selection, while no other rational explanation of their formation has ever been given.

Conclusion.

In concluding, the lecturer called attention to a series of cases which had shown us the actual working of natural selection at the present time. He also explained that these cases were at present few in number, first, because they had not been searched for; but perhaps mainly because they only occur on a large scale at rather long intervals, when some great and rather rapid modification of the environment is taking place.

In the following paragraph he endeavoured to summarise the entire problem and its solution:—"It is only by continually keeping in our minds all the facts of nature which I have endeavoured, however imperfectly, to set before you, that we can possibly realise and comprehend, the great problems presented by the 'World of Life'—its persistence in ever-changing but unchecked development throughout the geological ages, the exact adaptations of every species to its actual environment both inorganic and organic, and the exquisite forms of beauty and harmony in flower and fruit, in mammal and bird, in mollusc and in the infinitude of the insect tribes; all of which have been brought into existence through the unknown but supremely marvellous powers of Life, in strict relation to that great law of Usefulness, which constitutes the fundamental principle of Darwinism."

NOTICES OF BOOKS.

The Fundamental Principles of Chemistry. By WILHELM OSTWALD. Authorised Translation by HARRY W. MORSE. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1909.

THE difficulty of generalising in chemistry and laying the foundations of a rational scientific system without entering into details regarding the individual substances, is most successfully surmounted in this book, the sub-title of which, "An Introduction to all Text-books of Chemistry," clearly indicates its scope. Prof. Ostwald thoroughly understands the needs of the teacher, and takes an exalted view of the importance of educational work, and as is so often the case with his books it will be the teacher who is directly benefited by them, while the student will be only indirectly the gainer by the views and theories which he puts forward and for which he advances cogent arguments. The book both needs and merits careful reading, and every paragraph calls for the exercise of thought and reasoning power. The translation has been well done, and the English edition should find a place in every scientific library and on the shelves of every teacher of chemistry.

Foods: their Composition and Analysis. By ALEXANDER WYNTER BLYTH, M.R.C.S., F.I.C., F.C.S., &c., and MEREDITH WYNTER BLYTH, B.A., (Cantab), B.Sc. (Lond.), F.I.C., F.C.S., &c. Sixth Edition. London: Charles Griffin and Co., Ltd. 1909.

It would be unnecessary to do more than allude to the new features in the sixth edition of a work which is so well known and so deservedly appreciated as this standard textbook on the analysis of foods. The new matter includes sections on the identification of alcohols by means of their boiling-point, specific gravity, and the reactions of their derivatives; the paragraphs on the injurious effects of the higher alcohols are omitted. The testing of water by chemical and bacteriological methods is treated more fully than in the earlier edition, and many other additions have been made to the text. For instance, Vandani's method

of detecting the presence of cocoanut oil in butter, to which a short reference was made in the fifth edition, is now described in detail, and the tests suggested by other analysts for the same purpose are also discussed.

The Precious Metals, comprising Gold, Silver, and Platinum. By T. KIRKE ROSE, A.R.S.M., D.Sc. London: Archibald Constable and Co., Ltd. 1909.

A good introduction to the specialised study of the three precious metals, gold, silver, and platinum, is given in this book. The principle adopted is that of giving a very short outlined account of many methods of extraction and preparation rather than the full details of a more limited number; thus in the case of platinum, which is given the least space in the book, the Wollaston, Deville and Debray, and Matthey processes are all mentioned. The chemistry of the metals, their properties, compounds, and alloys are discussed, and general descriptions are given of methods of assay. Since the book is intended more or less for popular reading, special attention is paid to the history of the metals and their use, and some of the best and most interesting chapters are those on minting and the manufacture of gold and silver wares. For completeness sake the latest available statistics relating to the production and consumption of the metals are tabulated in the last chapter.

Practical Testing of Gas and Gas Meters. By C. H. STONE, B.S., M.S. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1909.

The first part of this book deals with photometry, and describes methods of conducting tests and of interpreting the results obtained, with special reference to legal requirements; the regulations in force in America are discussed most fully, though those of other countries are also mentioned. In Part II. the chemical testing of gas is treated, the determination of common impurities and gas analysis being described, although in outline only, an exhaustive treatment of the subject being thought unnecessary in a book of this character, which is written more for practical men, inspectors, and gas-works' managers than for the trained chemist. Parts III. and IV. cover calorimetry, the determination of specific gravity and pressure, and the testing of meters, with full accounts of standard forms of apparatus and their use. The book has been written mainly from the American standpoint, and will naturally have a wider circulation in that country than here, where there are many differences in procedure; however, its lucidity and practical spirit will appeal to the English gas-works' manager, who will find in it much information which is of value to him.

Forty-fifth Annual Report on Alkali, &c., Works. By the CHIEF INSPECTOR. London: Wyman and Sons, Ltd.

THE forty-fifth general report of the Chief Inspector of Chemical Works, containing copious statistics relating to the various processes which come under inspection, contains no features of special interest. The reports from different districts are included, and, incidentally, the details of the methods of analysis employed are stated. A further account is given of the Chief Inspector's investigation of coal carbonising, to which a short allusion was made in the forty-fourth report, the aim of the investigation being to throw some light upon problems connected with the carbonising of coal in continuous vertical retorts. The results of the research show that, both owing to want time and lack of sufficient laboratory equipment, it would be impossible for the subject to be thoroughly investigated in the Government laboratory, although important practical conclusions can be drawn as to the nature of the gaseous products.

CORRESPONDENCE.

THE IONIAN CULT.

To the Editor of the Chemical News.

SIR,—We the disciples of our Professor of Allerleiwissenschaft (the Science of Things-in-general or Business of knowing all sorts of things) are grateful to him for his frankness at the British Association. We now know, what some of us dimly suspected, that the Professor attributes more importance to his opinions and feelings than to his arguments. But is there not some danger in this knowledge reaching the multitude? Is it consistent with the business of being wise to give the show away? Will not even those patient animals "the British asses" (as Huxley called them) become a little restive? As long as they thought that they were being thrashed with good sound arguments submission appeared to be the better part of "the business." But may it not occur to them that their opinions and feelings are as powerful as those of the Professor, and equally good to kick withal? Among them are many benighted devotees of the Ionian cult, compared by the autocrat of the lecture-table, in one of his most charming utterances, with Christian scientists. Facts indeed seem to support their beautiful mare's nest, and figures to verify it. But we who hearken to the voice of the prophet crying in the wilderness know that there is nothing so misleading as facts except figures. Woe worth the day (as it is said in Saxon) when those wicked excursionists the physicists shall overrun our fair territory and render our science exact or even (Help! O genius of the English language) "quantifiable." We know, too, that as long as the Ionian heretics rely only on argument their fatal weakness is that they cannot explain everything, not even quantitatively. But once delivered from the incubus of argument, and undisciplined by our system and ritual, may they not use those natural weapons their opinions and feelings which even the barbarians possess? May there not be among them some horrid radicals, I mean radicles (or is it now radicyls?), who leaving the contemplation of the surface of things may go to explanatory extremes? Or worse still, may there not be among them some female scientists, more to be dreaded than Christian ones, since, as is well known, they almost rival our Professor in their disdain for logic and in the strength of their opinions and feelings?

The "business of knowing" will become intolerable. We shall all of us "cultivate and give expression to that state of mind which is the main qualification of the expert" (on this subject consult Huxley). There will be too many and too knowing professors.—I am, &c.,

SEE-OH-TOO!

UNIVERSITY OF LONDON APPOINTMENTS BOARD.

To the Editor of the Chemical News.

SIR,—It may be of interest to many of your readers to know that an Appointments Board has been constituted by the University of London. The terms of reference to the Board are "to assist graduates and students of the University in obtaining appointments, and to co-ordinate and supplement the work done by the schools and institutions of the University with this object." I am directed by the Board to express their hope that, through the medium of the Press, the objects of the Board may be brought to the notice of graduates as well as of those who are able and willing to assist in furthering the work of the Board, the aim of which is to encourage the selection of University men for all posts in the work of which the possession of a university training on scientific methods is an advantage. They wish to assist graduates to find employment, and to

assist employers to find, in the University ranks, suitable men for vacancies.

It would assist the Board if, whenever your readers know of any vacant appointments suitable for university men, they would communicate with the Secretary of the Board, so that he may put forward selected candidates. In this way the work of the Board as an employment exchange would be greatly helped.—I am, &c.,

HENRY A. MIERS, Principal.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlviii, No. 26, June 28, 1909.

Ordinary Carbon.—H. Le Chatelier and M. Wologdine.—The authors have performed many experiments in order to ascertain whether there are several varieties of ordinary carbon, which are the products of progressive polymerisations, and which have different densities and heats of combustion. They have found that in all varieties of ordinary carbon there is a considerable proportion of graphite, and they believe that there is only one variety of ordinary carbon of density about 1.8, the lower densities being due to the presence of included gases. It is not, however, possible to affirm with certainty the non-existence of several varieties of ordinary amorphous carbon.

Hydration of Potassium Carbonate.—M. de Forcrand.—Six hydrates of potassium carbonate have been described, viz., those with 4, 3, 2, $1\frac{1}{2}$, 1, and 0.5 H_2O . The only one which undoubtedly exists, or rather the only one which can always be prepared in ordinary conditions, is $K_2CO_3 \cdot 1.5 H_2O$. From experiments in which the heats of solution of K_2CO_3 and $K_2CO_3 \cdot 1.5 H_2O$ were determined, it appears that the hydrate with $1.5 H_2O$ is not a dehydrating agent, and for dehydrating purposes the anhydrous salt should be used. The use of K_2CO_3 for dehydration demands certain precautions. It is possible that hydrates with 3 or 4 H_2O exist at low temperatures.

Action of Metallic Oxides on Methyl Alcohol.—Paul Sabatier and A. Mailhe.—Some metallic oxides at temperatures below 400° reduce methyl alcohol by reactions which are analogous to those obtained with the primary alcohols. The catalytic decompositions effected by other metallic oxides are, however, rather different from those obtained with the primary alcohols. No hydrocarbon is formed but gaseous methyl oxide, which is soluble in water, and in concentrated sulphuric acid. The condensation of methyl alcohol over divided copper above 200° is less easily effected than that of the primary alcohols.

Comparison of the α -Rays Produced by different Radio-active Substances.—Mlle. Blanquies.—It is generally supposed that the α -particles emitted by different substances only differ in the velocity of their projection. If this is so, all α -particles ought to have the same properties if they are studied when at the same distance from the end of their path. In order to verify this the author has determined the shape of the ionisation curve in which the ionisation is expressed as a function of the distance; if the hypothesis is correct all the curves constructed on the same scale should be superposable. Using polonium, radium C, and actinium B the author finds that the curves of the two former agree very well, while that of actinium B is different. The difference can be satisfactorily explained by supposing that all α -particles are identical, except as

regards velocity of projection, but that the radiation obtained by using as source a plate rendered active by contact with actinium emanation is complex. The experimental investigation of this hypothesis does not perfectly confirm it, but, on the other hand, the curves are not known with absolute certainty, so that complete agreement cannot be expected.

Bromide of Dimercury-Ammonium, NHg_2Br .—H. Gaudechon.—When a hot solution of $HgBr_2$ is added to a cold solution of ammonia a white precipitate of $NHg_2Br \cdot 3NH_4Br$ or a yellow precipitate of $NHg_2Br \cdot NH_4Br$ is obtained according to the concentration. When either of these is washed with water, $NHg_2Br \cdot H_2O$ is obtained. If, however, the ammonia solution is added to the hot $HgBr_2$ solution, a precipitate is formed, which on washing does not give $NHg_2Br \cdot H_2O$. This precipitate appears to be a compound $(NHg_2Br)_4 \cdot HgBr_2$ analogous to $(NHg_2Cl)_4 \cdot HgCl_2$. From this NHg_2Br is obtained by treatment with ammonia. It is a yellow crystalline substance which explodes when rapidly raised to a red heat. When slowly heated it decomposes into mercurous bromide and mercury. It very slowly absorbs water from damp air, $NHg_2Br \cdot H_2O$ being formed. The reverse reaction, i.e., the conversion of the hydrate into the anhydrous salt, has not yet been performed.

Formation of Oxygen Compounds of Nitrogen and their Metallic Compounds in the Production of Ozone for the Sterilisation of Water.—Ed. Bonjean.—In large installations for ozonising air appreciable amounts of oxides of nitrogen are formed, and the author has succeeded in determining the successive stages of their formation. Ferric oxide is first formed without nitrification. The oxide thus formed in the finely divided state favours the production of nitrous vapours, which are then transformed into nitric acid, and attack the lead or iron of the ozonisers. Hence the use of these metals should be altogether avoided.

Separation of Graphite in Cast-iron Heated under Pressure.—Georges Charpy.—It is known that the carbon combined with iron in cast-iron which is rapidly cooled separates in the form of graphite when the metal is heated to 600 – 700° . By constructing a suitable apparatus by means of which the pressure could be raised to about 15,000 atmospheres, the author has found that in these circumstances the carbon obtained by the decomposition of iron carbide at temperatures from 700 – 1100° also separates in the form of graphite.

Uranyl Chloride.—Æchsner de Coninck.—Uranyl chloride may be obtained by adding drop by drop a solution of barium chloride to a concentrated freshly prepared aqueous solution of uranic sulphate:— $SO_4(UO_2) + BaCl_2 = BaSO_4 + UO_2Cl_2$. The compound is deliquescent and dissolves in water. When reduced by hydrogen it yields HCl and UO_2 . When heated with a large excess of caustic potash in an open tube a peruranate is formed:— $UO_2Cl_2 + 2K_2O + O = 2KCl + UO_5K_2$. With barium chloride and ammonia it yields barium uranate:— $UO_2Cl_2 + BaCl_2 + 4NH_3 + 2H_2O = 4NH_4Cl + UO_4Ba$.

Lactonisation of Acid-alcohols.—E. E. Blaise and A. Koehler.—By three successive reductions of the corresponding ketone acids with zinc and potash in presence of platinum, the two acids $C_2H_5-CHOH-(CH_2)_4-CO_2H$ and $C_3H_5-CHOH-(CH_2)_5-CO_2H$, can be prepared. The former when slowly distilled *in vacuo* gives ϵ -octolactone, and by dehydration with sulphuric acid it gives γ -lactone, i.e., γ -*n*-butylbutyrolactone. Apparently sulphuric acid of suitable strength always gives a lactone when it acts upon an acid alcohol or an ethylenic acid, whatever the position of the alcoholic function or of the double bond in the original molecule. With the second acid the results are somewhat different, no lactone being formed when it is distilled *in vacuo*. With sulphuric acid α - γ -lactone is again obtained, viz., γ -*n*-amylbutyrolactone.

THE CHEMICAL NEWS.

VOL C., No. 2601.

NEW METHOD OF PRODUCING A CADMIUM ARC.*

By T. MARTIN LOWRY, D.Sc. F.C.S.

IN order to produce a cadmium spectrum of sufficient intensity for polarimetric work advantage is taken of the favourable properties of the silver-cadmium alloys. On account of their isomorphism the two metals form an excellent series of alloys which are characterised by good mechanical properties and very high melting-points. (An alloy with 60 per cent Cd melts as high as $700^{\circ}\text{C}.$). In striking contrast to the behaviour of the pure metal the alloy gives a steady arc which can be kept true to centre by rotating the electrodes in opposite directions. The spectrum shows the silver as well as the cadmium lines, but these are so far separated that even with a low resolving power the slit of a spectrocope can be opened to its full width without any overlapping of the brilliant "blocks" of light which take the place of the usual "lines."

ON THE CONSTANCY OF THE HYDROGEN GAS ELECTRODE.*

By CHARLES J. J. FOX, B.Sc., Ph.D.

THE author has investigated the constancy of the hydrogen gas electrode in H_2SO_4 and HCl , when gold, platinum, and palladium coated with platinum black and with palladium black are employed. Palladium coated with palladium black gives in both $0.1\text{N}\text{H}_2\text{SO}_4$ and $0.1\text{N}\text{HCl}$ a value 4 to 5 millivolts too high; which is permanent even when the hydrogen is allowed to pass over the electrode for hours. But gold and platinum coated with either platinum or palladium black give in a very few minutes in both HCl and H_2SO_4 , values concordant among themselves to probably less than 0.05 of a millivolt. A piece of gold or platinum wire is as good as a large piece of foil. It has usually been considered that the hydrogen gas electrode in $0.1\text{N}\text{HCl}$ is not so constant as in $0.1\text{N}\text{H}_2\text{SO}_4$. But this does not seem to be the case; at all events if precautions against the possible presence of arsenic be taken. It seems probable from Bredig's work that the smallest trace of arsenic would "poison" the platinum or palladium black, and according to Crookes ("Select Methods of Analysis," 1905, p. 564) it is practically impossible to purchase HCl free from arsenic. When this is borne in mind it seems preferable to use $0.1\text{N}\text{HCl}$ rather than H_2SO_4 , because the dissociation constant is so much better known and the ions produced are much simpler. It is not possible to get a good coating of platinum black on a very pure specimen of platinum foil if the platinum chloride solution employed be also very pure. A trace of lead acetate is usually added to the solution therefore, and it is necessary to remove every trace of this from the electrode after coating, or good values will be unobtainable. Heating in a solution of oxalic acid and then in nitric acid removes all lead quite satisfactorily.

Cementation of Iron by Carbon in Vacuo.—Léon Guillet and Ch. Griffiths. —The authors' experiments on the cementation of iron by pure carbon show there is no cementation if precautions are taken to prevent the presence of gases, but it takes place if contact is ensured. Moreover, it increases with the pressure, but always occurs extremely slowly.—*Comptes Rendus*, cxlix., No. 2.

* A Paper read before the British Association (Section B), Winnipeg Meeting, 1909.

NOTE ON THE APPLICATION OF POLARISED LIGHT TO DETERMINE THE CONDITION OF A BODY UNDER STRESS.*

By Professors S. P. THOMPSON, F.R.S., and E. G. COKER.

THE application of polarised light to observe optically the strained condition of glass and other transparent materials when subjected to stresses has been known since the days of Brewster and Biot. When an ordinarily isotropic body, such as glass, is subjected to pressure or tension, it becomes, in fact, doubly refractive, the axis of double-refraction being along the line of maximum stress; and the presence of such double-refraction is made evident by examining in the polariscope the light transmitted through the object.

Hitherto the usual disposition has been the following:—An ordinary polariser, such as a large Nicol prism, or a black-glass reflector set at the polarising angle, is employed to produce plane-polarised light. An ordinary Nicol prism is used as analyser; and habitually their principal planes are crossed so as to produce the dark field. Then the piece of glass to be examined is placed between them, and means are provided, by pinching screws or compressors, to subject the glass to stresses in a plane normal to the axis of the beam of light through the Nicols. No effect is produced if the axis of double-refraction, that is, the axis of the strain, lies parallel to the plane of polarisation of either the polariser or the analyser. If the axis of double-refraction is at all oblique to such plane, then more or less light is transmitted. As a result of this disposition the apparent amount of light seen through the polariscope varies according to the square of the sine of half the angle which the axis of stress makes with the plane of polarisation of the polariser; and the observed figure in the stressed specimen changes if it is rotated in its own plane in the instrument. This is further complicated, if the light be not monochromatic, by the chromatic differences in the double-refraction. Again, as is well known, and as a result of this maximum effect at 45° , if any object be taken in which the stresses are radial in direction—as is the case when a short cylinder or circular disc of glass has been subjected to sudden cooling, so that the peripheral portion contracts with great force upon the central portion—the object exhibits in the polariscope a black cross with its pairs of arms respectively parallel to the planes of polarisation of polariser and analyser, the light being a maximum in directions at 45° between the arms of the black cross. These arms remain fixed, even though the object be rotated in the apparatus. If other objects are used in which these naturally occur, equal strains will apparently produce unequal effects, because the different parts cannot be so placed that everywhere the axis of strain shall be all at the same angle with the principal axis of the apparatus, and there is an optical inequality, due to the very arrangement of the polariscope that does not correspond to any inequality in the specimen, or in the forces to which it is subjected.

Furthermore, in order to produce any very evident effects in glass, either the specimen must be very thick (as is the case of the pieces of unannealed glass generally employed in polariscopic demonstrations) or else the forces to which the glass is subject by the compressing screws must be so great as to come perilously near to breaking the object. Indeed, it is quite common in the ordinary apparatus for showing these effects for the little bars or squares of glass to be broken or crushed in showing the experiment.

Two things, therefore, need to be done in improving the means for studying and exhibiting optically the stresses in transparent solids:—(1) To use a material more compressible than glass; (2) to devise optical means for getting rid of the black cross, and of making the optical effect independent of the particular angle at which the specimen, or any part of it, might be placed.

* A Paper read before the British Association (Section G), Winnipeg Meeting, 1909.

The first of these ends was obtained by the adoption of a particular kind of xylonite instead of glass. Xylonite is a preparation of nitro-cellulose in commercial use. It is not quite as transparent as glass, but it is transparent enough, even when of a thickness of 10 mm., to be entirely useful. It is slightly tinted and slightly turbid. Sheets 3 or 4 mm. thick are practically transparent. From such sheets or selected portions of sheets the objects to be experimented upon are cut out.

The second improvement, which is entirely successful in eliminating the black cross, and in rendering the optical effect independent of the position of the specimen in the field, we have effected by the device of substituting circularly-polarising apparatus for both analyser and polariser. To this end we take two thin plates of mica (or of quartz cut parallel to the axis of crystallisation), selected so as to give as nearly as possible a retardation of one quarter-wave length for yellow light (D-line) between their ordinary and extraordinary rays. For many purposes ordinary so-called "quarter-wave plates" will suffice; but the ordinary quarter-wave plates, as sold, differ considerably amongst themselves; and it is important that the pair chosen should be alike in optical property. One must be large, covering the whole field of view; the other may be quite small. The larger quarter-wave plate is placed between the polariser and the object, and is preferably attached to the polariser. It is set with its own axis at 45° to the plane of polarisation of the polariser. Thus set it transmutes the plane-polarised beam into a circularly-polarised beam. The cheirality of this beam is right-handed or left-handed according to whether the axis is set at 45° to the left or at 45° to the right. The smaller quarter-wave is placed between the object and the analyser, and is preferably attached to the front of the analysing Nicol, to rotate with it, if the Nicol is turned. It also must be set with precision with its own axis at 45° to the plane of polarisation of the Nicol. If it receives a beam of circularly-polarised light it transmutes that beam into plane polarised light, and this is either cut off or transmitted by the analyser, according to whether its own axis is at 45° to the left or to the right; or, in other words, according as to whether the cheirality of the analysing combination of quarter-wave and Nicol is opposed to, or concordant with, the cheirality of the polarising combination.

If the quarter-waves are so set as to give "dark field," then there will still be dark field even if the analysing combination be rotated through any angle. Or if they are so set as to give "bright field," then there will still be bright field for every position of the analysing combination. With this apparatus one cannot change, as in the ordinary polariscope, from "dark field" to "bright field" by turning the analyser through 90° . To do this requires that one or other of the quarter-waves must be rotated in its own plane through 90° , or be reversed face for face by turning through 180° around an axis parallel to the plane of polarisation of the Nicol with which it has been combined.

With the above disposition of circular polariser and circular analyser, we get rid entirely of the black cross; and, further, with the exception of certain slight changes of tint, the optical appearance of any polarising object placed in the apparatus remains invariable at whatever angle that object may be placed in the field.

Acylation of Amines.—Hartwig Franzen.—If the hydrochloric acid salt of an amino-derivative is suspended in benzene, and benzoyl chloride is added, on heating the acyl-derivative is obtained almost quantitatively according to the equation $R.NH_2.HCl + R.CO.Cl = R.NH.CO.R + 2HCl$. An acid anhydride can be used instead of the acid chloride. This method of acylating amines is very quick and convenient, and the author has applied it to the preparation of many derivatives.—*Berichte*, xlii., No. 11.

"CORK METAL."

By F. J. WILLOTT.

At one of the recent aeronautical exhibitions, samples of a metal were shown under the name of "cork metal," which was said to be 40 per cent lighter than aluminium, and to have numerous other properties which should make it a rival of the latter.

Great secrecy was maintained as to the nature of this wonderful metal, but its properties were such as to rouse my interest, as a consequence of which I have submitted it to chemical analysis.

In appearance the metal resembles very strongly the alloys known as magnalium. The surface presents a lustreless whitish grey colour, both sheets and bars showing the scorings and scratches so frequently found on badly rolled or drawn aluminium. Careful analysis gave the following result:—

Aluminium	0.04	per cent
Iron	0.017	"
Zinc	0.48	"
Sodium	0.21	"
Magnesium	99.30	"

It will be seen therefore that essentially "cork metal" is nothing but magnesium to which a small amount of zinc has been added. Whether this latter has been purposely introduced or, as is more probable, is merely present as an impurity, I am unable to say.

As the metal evolves hydrogen when immersed in water, I found it necessary to use organic solvents for the determination of the specific gravity. In alcohol this was found to be 1.762, thus confirming the conclusion that cork metal is, in fact, magnesium.

THE ESTIMATION OF GRAPHITE.

By FRANK BROWNE, F.I.C., Government Analyst, Hongkong.

In a previous paper (CHEMICAL NEWS, xcvi., 51), it was shown that the amount of carbon in graphite could easily be ascertained by means of a specially prepared iron oxide. The examination of a sample of "Acheson" graphite has confirmed the previous statement that the oxide of iron remains at the end of the estimation in the same condition as at the commencement. The results of five experiments are recorded below. When one experiment was concluded, another weight of graphite was put into the used oxide, and so on for the series.

Weight of graphite taken.	Gain in weight of iron oxide.	Percentage of mineral matter indicated.
Grm.	Grm.	
0.9912	0.0015	0.1513
1.1197	0.0016	0.1429
1.3920	0.0025	0.1796
1.5308	0.0020	0.1306
1.7247	0.0028	0.1623

By direct and long incineration of the graphite itself the percentage of mineral matter was found to be 0.1580.

It was found that the prepared iron oxide after having been kept a year was still serviceable. Five grms. of such heated in an open crucible to a pale red for an hour did not thereafter alter in weight, and was quite ready for an estimation.

The "Acheson" graphite—grade No. 1340, as made in the electric furnace—was kindly supplied by the International Acheson Graphite Company, Niagara Falls, N.Y., U.S.A. Containing 0.158 of mineral matter and 0.170 of water, its purity was 99.672 per cent.

EXTRACTION OF LUTECIUM FROM THE EARTHS OF GADOLINITE.

By MM. G. URBAIN, BOURION, and MAILLARD.

LUTECIUM was isolated for the first time from xenotime (G. Urbain, *Comptes Rendus*, Nov. 4, 1907).

In this article we shall describe the methods by which we have extracted the element from the earths of gadolinite, and separated it from the scandium and thorium which accompany it in this mineral.

We started with yttric earths of atomic weight 118, which had been approximately separated in a factory from the earths of the ceric group, and which had been roughly fractionated as chromates (Moissan and Etard, *Comptes Rendus*, 1896, cxxii., 573) to eliminate the greater part of the yttrium which is present in large quantities in the original material. These earths consisted chiefly of yttrium, but they also contained the greater part of the erbium and the ytterbium in the mineral. Moreover, they included an appreciable amount of earths of the ceric group. These latter were present in so small a proportion that we thought it was useless to undertake a preliminary treatment to eliminate them, and the whole of the material was fractionated by the crystallisation of the simple nitrates with five molecules of water in nitric acid.

Thus we rapidly obtained almost uncrystallisable mother-liquors, which were very impure, and contained the greater part of the neoytterbium and all the lutecium of the original material. As lanthanum and cerium were also concentrated in these fractions we first tried to eliminate them by potassium sulphate, but we were obliged to abandon this method, which was too rough. Magnesium nitrate was then added to the nitrates, and enough bismuth magnesium nitrate to obtain on cooling a large quantity of crystals of the double nitrates.

The double nitrates of cerium-lanthanum and magnesium are insoluble in the saturated solution of the double nitrate of bismuth and magnesium, and after two or three similar purifications no trace of ceric earths which can be detected spectroscopically is left in the liquors.

This method can be recommended both on account of the results obtained and for the ease with which it can be performed.

Precipitation with water after the elimination of the excess of acid and subsequent treatment with sulphuretted hydrogen removes the bismuth; precipitations with ammonia in presence of ammoniacal salts eliminate the magnesium. The lutecium earths are then precipitated with oxalic acid.

These earths contained besides lutecium and neoytterbium a considerable amount of erbium and yttrium. New crystallisations of the simple nitrates removed them from the first fractions. The lutecium was concentrated in the most soluble fractions, and after a hundred series of crystallisations, the last fraction had become fairly large and refused to crystallise. The earth extracted from it exhibited very feeble paramagnetism.

It was converted into chloride by the method described by one of us (Bourion, *Comptes Rendus*, Jan. 18, 1909), a process which consists in heating the oxide in an atmosphere of sulphur chloride. Thus a fairly abundant sublimate of white crystals was formed. This sublimate was collected and submitted to a spectrographic examination. It consisted of a mixture of thorium chloride and scandium chloride. The non-volatile chloride was then heated to a high temperature in a porcelain tube, through which a current of chlorine was passed. In these new conditions the lutecium chloride began to sublime. It is much less volatile than the chlorides of scandium and thorium, and can easily be separated from them owing to this difference; it is decidedly more volatile than the chloride of neoytterbium. This difference enables small quantities of lutecium to be removed from large quantities of neoytterbium, but it is more difficult to separate large quantities of lutecium from small quantities of neoytterbium.

However, we have in this method a new means of separating the two elements as chlorides by fractional sublimation.—*Comptes Rendus*, cxlix., 127.

A NEW METHOD OF SEPARATING URANIUM X AND ITS RELATIVE ACTIVITY.

By S. SZILARD.

In the course of a series of experiments (*Le Radium*, 1909, p. 80), carried out in Madame Curie's laboratory, I found that if barium sulphate is precipitated in solutions of radio-active substances the presence of iron favours the separation of certain active products; more recently I found that barium sulphate precipitated by reagents which had been carefully freed from traces of iron, in a solution containing neither iron nor uranium, carries down very little uranium X, and that it carries down more in presence of uranium, and still more when iron is also present.

Moreover, I noticed that the precipitate obtained with iron, especially the hydrate, in a solution of radio-active substances carries down certain of them (polonium, radium, &c.). Moore and Schlundt (*Le Radium*, 1906, p. 332) had already shown that if the uranium X is separated from the uranium by means of acetone, the addition of iron hydrate increases the yield. I have endeavoured to find a new method of separating uranium X based upon these observations.

I tried to effect the precipitation of the iron hydrate in the uranium solution, and I showed that the yield is greatest if a solution of iron acetate and uranyl acetate is decomposed by heat.

The precipitate thus obtained contains the greater part of the uranium X of the uranic solution; however, the yield depends upon the acidity of the liquid. When the solution is very slightly acid (acetic acid) the yield of uranium X is greater, but the precipitate also contains uranium; on the other hand, if the solution is too acid the precipitate will contain only exceedingly little uranium, but at the same time it will be less rich in uranium X.

The following method may be adopted:—50 grms. of uranyl acetate are dissolved in 1 litre of lukewarm distilled water and a solution containing ferric acetate, ammonium acetate, and acetic acid is then added. (Instead of the acetate the nitrate can be used, but in this case more iron is needed to obtain the same yield, and it is best to mix a little ammonium carbonate with the solution). The liquid is heated, and is kept boiling for some minutes; filtration is begun at once, and should be quite completed while the liquid is still hot. The precipitate is carefully washed with hot water, and then with a solution of ammonium carbonate.

The uranium X can be concentrated, the precipitate being re-dissolved in acetic acid and partially re-precipitated by the same process.

A better method of concentration consists in dissolving the precipitate in hydrochloric acid, and then shaking this solution with a large quantity of ether free from alcohol; the ether dissolves the greater part of the iron, the quantity of which dissolved in some drops of water can be reduced to a minimum by repeating the extraction with ether. The greater part of the uranium X will always remain in the water.

The yield is greater than that obtained by methods previously known, but it is not total. In every case with a single operation it is easy to obtain per grm. of uranium a product giving in a cylindrical condenser an ionisation current equal to that given by 0.03 grm. of uranium in equilibrium. The dimensions of the condenser are:—Height 25 cm., radius 7 cm., radius of plate on which the substance is placed 3 cm.

I have used this method to determine the relation between the ionising power of uranium X and that of uranium when these two substances are in radio-active equilibrium.

Theoretically by repeating the precipitations at intervals of a day the precipitation of the uranium X may be considered complete if the activity of the last precipitate is about 2.5 per cent of the total activity of the products previously obtained.

Practically on repeating the precipitations twelve times the activity of each of the four last fractions is about the same and equal to 4 per cent of the total activity of the products. The last traces of uranium X are evidently very difficult to separate from uranium, a phenomenon which has already been observed by H. Becquerel. The number that can be obtained is thus only approximate.

Taking into account the traces of uranium carried down in the precipitates (the amount of uranium is determined by an experiment), it is found as the mean value of two series of measurements that the ionisation current produced by uranium X in radio-active equilibrium with 1 grm. of uranium is equal to that produced by 0.237 grm. of uranium in radio-active equilibrium. To take into consideration the radiation which was not used in the condenser employed I have relied upon our approximate knowledge of the law of the absorption of the rays in air.

If it is assumed that the number of atoms decomposed per grm. of uranium per second is about the two-millionth part of the same number for radium, we find that 1 grm. of uranium in radio-active equilibrium contains about 2×10^{-11} grms. of uranium X, the total activity of which is equal to that of 0.237 grm. of uranium in equilibrium.

Uranium X in a state of purity would then be about ten thousand million times as active as uranium in radio-active equilibrium.—*Comptes Rendus*, 1909, 113.

THE ESTIMATION OF IRON BY PERMANGANATE IN PRESENCE OF HYDROCHLORIC ACID.*

By G. CECIL JONES, A.C.G.I., F.I.C., and JOHN H. JEFFERY.

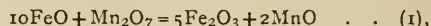
IN most text-books of analytical chemistry, two methods are described for the estimation of iron by permanganate in presence of hydrochloric acid—namely, the method of Fresenius and that of Zimmermann-Reinhardt. Within the last year or so doubt has been cast on both these methods, Harrison and Perkin (*Analyst*, 1908, xxxiii., 47), as a result of their experiments with the Zimmermann-Reinhardt method, expressing the view that "for exact titrations permanganate cannot be employed in presence of hydrochloric acid," whilst Birch (*CHEMICAL NEWS*, 1909, xcix., 61 and 73) was unable to confirm the results of Fresenius.

Had we felt that Harrison and Perkin were justified in their conclusion, this paper would never have been written; but their work certainly showed that very inaccurate results might be obtained by following Treadwell's description of Reinhardt's method, and suggested that the excellent results published by earlier authors might have been due to a happy balance of opposing errors. On the other hand, it remained possible that the other workers had, in their experiments, secured constancy of certain conditions, the importance of which they did not realise or at least failed to emphasise. We set ourselves the task of determining whether any set of conditions, reasonably attainable, would render the Zimmermann-Reinhardt method of universal application, whilst we were led to study Fresenius's method by the recommendation given to it by Hehner during the discussion of Harrison and Perkin's paper.

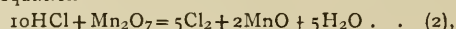
It will be convenient to review briefly, in the light of our present knowledge, the history of these methods, more especially as that of Fresenius, though supported for a generation by his great name, finds little or no support in the experiments which he describes.

When Marguerite (*Ann. Chim. Phys.*, 1846, xviii., 244) first recommended the use of permanganate for the volumetric

determination of iron, it was supposed that the reaction proceeded quantitatively in accordance with the equation—



whether the titration was conducted in presence of sulphuric acid or of hydrochloric acid. Löwenthal and Lenssen (*Zeit. Anal. Chem.*, 1862, i., 329) were the first to show that, in the presence of hydrochloric acid, the consumption of permanganate was excessive, and that this was due to its being used up in oxidising hydrochloric acid in accordance with the equation—



a reaction which proceeds but slowly in pure dilute solutions, but which is greatly accelerated by the presence of iron salts. There is some evidence to-day that the reaction may be less simple than is indicated by Equation 2, but the net result of the possible series of reactions is reduction of permanganate and liberation of chlorine, some of which escapes reduction by the ferrous iron, the exact amount of such escape depending on the conditions of the experiment. From a study of the results of Löwenthal and Lenssen, which he repeated and confirmed, Fresenius (*Zeit. Anal. Chem.*, 1862, i., 361) was led to recommend the method known by his name. His experiments were of this kind:—He found that 25 cc. of N/10 ferrous solution, diluted to a litre with water containing some 30 cc. of hydrochloric acid (specific gravity, 1.1), required the addition of something like 26 cc. of N/10 permanganate before the pink tint of the latter became permanent. If, then, a further 25 cc. of ferrous solution was added to the contents of the flask or basin and the titration continued, not much more than 25 cc. of permanganate was usually necessary to restore the pink colour, whilst a third addition of ferrous solution almost invariably required exactly 25 cc. of permanganate. On the strength of these experiments, Fresenius recommended that, where titration in presence of hydrochloric acid was unavoidable, the iron solution should be made up to 250 cc., 50 cc. of this diluted with a large volume of water, and permanganate added until a permanent pink resulted, when a further 50 cc. of the iron solution was to be added and titration continued, and so on. When two consecutive and closely concordant numbers were obtained, the mean of these was to be taken as the true reading for 50 cc. of the iron solution. According to Fresenius, the third and fourth numbers should always, and the second and third usually, agree well together, but he gives no practical example of the application of this, his first, method. A second method, where but a small quantity of the ferrous solution was available, was to add to a considerable volume of water, acidified with hydrochloric acid, some 25 cc. of N/10 ferrous solution and just sufficient permanganate to produce a permanent pink tint, and then to pour into this mixture the liquid to be analysed, when titration with permanganate was said to give a fair result. Two examples of this method were given, but we show later that an important condition was realised in these experiments which would never be the case in any practical attempt to apply the method.

Kessler (*Pogg. Ann.*, 1863, cxix., 225) recorded the fact that in the presence of much sulphuric acid, and still more in that of manganese sulphate, the disturbing influence of hydrochloric acid is greatly reduced; but it remained for Zimmermann (*Annalen*, 1882, ccxiii., 305; also *Ber.*, 1881, xiv., 779) to recommend the use of manganese sulphate as an aid to accuracy of analysis. He stated that, if at least 1 grm. of the crystallised salt were taken for each 15 cc. of hydrochloric acid (specific gravity, 1.1) supposed to be present, iron might be titrated as accurately in hydrochloric as in sulphuric acid solution. Reinhardt (*Chem. Zeit.*, 1889, xiii., 323) replaced the simple manganese sulphate solution of Zimmermann by a solution made by dissolving 200 grms. of the crystallised salt in 1000 cc. of water, and adding to this a cooled mixture of 400 cc. concentrated sulphuric acid, 600 cc. water, and 1000 cc. phosphoric acid (specific gravity, 1.3). The

* From the *Analyst*, July, 1909.

use of this solution, of which Reinhardt took 60 cc. for each experiment, renders the assay liquid practically colourless until the permanent pink tint due to permanganate announces the completion of the titration. In the absence of phosphoric acid, the yellow colour of ferric chloride renders the end-point less clear. The addition of phosphoric acid to the manganese sulphate appears also to increase slightly the efficiency of the latter as a retarder of chlorine evolution. Reinhardt says nothing concerning the accuracy of the method.

Since the introduction of Reinhardt's modification of Zimmermann's method, it has been usual to speak of titrations conducted in absence of hydrochloric acid, and in which Marguerite's Equation 1 is strictly fulfilled, as being carried out according to Marguerite, and the use of the expression "Marguerite's method" in this restricted sense will save much verbal repetition in the paragraphs which follow.

Treadwell ("Analytical Chemistry," English edition, vol. ii., 483), who makes use of Reinhardt's solution, states that the amount of manganous salt present should not exceed the amount of iron to be estimated. We have been unable to discover any publication of his in which he gives grounds for this statement, but possibly it was the result of an experience similar to that of Harrison and Perkin. These authors (*loc. cit.*) found that Reinhardt's solution itself may exert an oxidising action on ferrous solutions, and so reduce the permanganate consumption; and that this oxidising power is not even constant, but is in some way dependent on the age of the solution. The results they obtained by following Treadwell's directions varied considerably, but were all too high, and the best of them were found to owe their relative accuracy to the oxidising power of the newly prepared Reinhardt solution. Working with older manganese solutions, they found the over-consumption of permanganate as much as 0.8 cc. with only 15 cc. of hydrochloric acid (specific gravity, 1.1) present, and the over-consumption increased with increasing concentration of hydrochloric acid.

On the other hand, Brandt (*Chem. Zeit.*, 1908, xxxii., 812, *et seq.*) gives tables showing that in his hands the method of Reinhardt yields results which, if not wholly independent of the amount of hydrochloric acid present, are at any rate not greatly influenced by much larger quantities than those employed by Harrison and Perkin. The main purpose of his paper is the recommendation of pure ferric oxide as a standard for determining the titre of permanganate solutions intended for use in estimating iron by the Zimmermann-Reinhardt method, and, if this substance be adopted as the standard, dissolved in hydrochloric acid and reduced by stannous chloride precisely as an ore would be treated, he says that method leaves nothing to be desired. His experiments show that, under the conditions which prevail in his practice, and with iron equivalent to about 50 cc. of a decinormal solution present, the permanganate consumption is almost exactly 0.2 cc. greater than is required by Marguerite's equation. For routine analysis, where approximately the same reading—40 to 50 cc.—can be obtained in every experiment, no correction is necessary if ferric oxide be adopted as the standard. His paper provides no answer to the criticisms of Harrison and Perkin concerning the alterability of Reinhardt's solution, and it is strange that he did not think to vary the amount of iron in his experiments, which give one no hint as to the interpretation to be placed on a reading of a different order of magnitude, say, 2.5 cc. If 0.498 gm. of pure ferric oxide, reduced and titrated by Reinhardt's method, gives a reading of 50 cc., to how much ferric oxide does a reading of 2.5 cc. correspond? One-twentieth of 0.498 is 0.0249, or, say, 0.025; but Brandt tells us that the error of the method, as compared with that of Marguerite, is 0.2 cc. when there is ferrous iron present equivalent to 0.498 gm. of ferric oxide, and the error will surely not be less when the concentration of iron is reduced, and that of hydrochloric acid maintained constant. It would seem more reasonable to suppose that 2.5 cc. was equivalent to 0.023 gm. ferric

oxide, and without experiment no one would care to assume that it had a value even so high as this. Now, the difference between 0.025 and 0.023 is a matter of 10 per cent, far too large an amount to be left in doubt.

To the iron and steel worker these considerations will have no weight. He can insure a reading of 40 to 50 cc., and, moreover, is too expert in the use of bichromate to heed our results or Brandt's; if, indeed, he has not as a rule a method of his own for applying permanganate. With the general worker it is far otherwise. He is called upon to estimate widely varying quantities of iron in materials as to the composition of which he knows very little in advance; and there is no doubt that he would, as a rule, prefer to use permanganate were he sure that it would give him accurate results, and it is to such as he that this paper is addressed.

(To be continued)

THE ELECTRICAL PROPERTIES OF FLAME.*

By Prof. HAROLD ALBERT WILSON, M.A., D.Sc., F.R.S.

If a flame is brought near to an insulated conductor charged with electricity, the charge disappears. This is explained by supposing that the gases in the flame are partially dissociated into ions. A neutral molecule splits up into two ions, one having a negative charge and the other a positive charge. The conductor, if positively charged, attracts the negative ions out of the flame, and their charges when they reach it neutralise its charge.

If a plate of an insulator, such as ebonite, is placed between the flame and the charged conductor, the ions are still attracted through the plate; but when they reach it they cannot get through, and so remain on its surface. The side of the plate turned towards the flame thus gets a charge of opposite sign to that on the conductor. This shows that the disappearance of the charge in the first case was due to an opposite charge attracted out of the flame, and not to the charge on the conductor escaping into the flame.

We have a stream of gas rising from the flame, and the ions go up in the stream. The ions of opposite sign attract one another, and when two come together their charges are neutralised, and the two ions are said to have disappeared by re-combination. Thus, as we go up in the stream of gas from the flame the number of ions diminishes. If the stream of gas is allowed to pass up a long tube containing along its axis a series of charged electrodes, then the bottom electrode will be discharged first, and then the next one, and so on. The ions are used up in discharging the electrodes, so that the electrodes are discharged in order, beginning with the lowest one. When the lower electrodes have been discharged, the upper ones begin to be discharged, but more slowly, because many of the ions disappear by re-combination before they get far up the tube. Another effect also comes in; as the gases cool down the ions do not move so freely through them, and so are not so easily attracted by the electrodes. This makes the rate of discharge of the upper electrodes still slower.

Thus, as we go down towards the flame the number of ions and their mobility rapidly increases, and right inside the flame the number is so large that the flame behaves like a good conductor of electricity.

If the terminals of an induction coil are connected to two Bunsen burners, sparks can be passed from the tip of one flame to the tip of the other. The temperature of the flame is about 2000° C., so that the density of the gases in it is about one-seventh of their density at the ordinary temperature. The potential difference required to send a spark through the flame is about the same as that required to send a spark through an equal length of air at one-seventh of ordinary atmospheric pressure. It appears therefore that the ions do not make it easier for a spark to

* A Discourse delivered before the Royal Institution, February 12, 1909.

pass. This is due to the fact that the current in the spark is greater than the ions can carry, so that the potential difference has to be enough to produce more ions, and so is the same in the flame as in unionised air at the same density.

To study the conductivity of flame, it is convenient to use a row of small Bunsen flames placed so that they touch each other. I use a row of fifty flames burning from quartz tubes 1 cm. apart. This gives a flame 50 cm. long, and about 10 cm. high. The quartz tubes insulate very well, so that a current can be passed along the flame horizontally from one end to the other.

If two parallel platinum electrodes immersed in the flame are connected to a galvanometer and battery, it is found that a measurable current is obtained. The relation between the current (i) and the difference of potential (V) between the electrodes is given by the equation $V = Ai^2 + Bdi$, where A and B are constants and d denotes the distance between the electrodes. If d is small, say, 1 or 2 mm., the term Bdi is negligible (except when i is very small), and we get $V = Ai^2$. In this case the current is almost independent of the distance between the electrodes.

The reason for this peculiar relation between the current and potential difference becomes apparent when the variation of the potential along the flame from one electrode to the other is examined. An electrometer is connected to two platinum wires, which are immersed in the flame and can be moved along horizontally between the electrodes. Each wire takes up the potential of the flame at the point where the wire is situated, so the deflection of the electrometer indicates the difference of potential between the two points where the wires are put in. Suppose one wire is allowed to touch the positive electrode and the other is gradually moved along the flame from the positive to the negative electrode. It is found that in the space between the electrodes there is a small uniform potential gradient, but near each electrode there is a comparatively sudden drop in the potential. The drop near the negative electrode is much larger than the drop near the positive electrode. Thus, nearly all the electromotive force of the battery is used up close to the negative electrode. This shows that nearly all the resistance offered by the flame to the passage of the current is close to the negative electrode. The positive ions in the flame move towards the negative electrode and the negative ions towards the positive electrode; in fact, the current is carried through the flame by these two streams of ions. Hence, close to the negative electrode the current must be carried entirely by positive ions moving towards it, and at the positive electrode the current must be entirely carried by negative ions. We find that the resistance near the negative electrode is much greater than near the positive electrode, so that we conclude that the negative ions carry the current more easily than the positive ions. With a given electric force, the negative ions move very much faster than the positive ions. It has been shown experimentally that the velocity of the negative ions is about 10,000 cm. per sec. for one volt per cm., while that of the positive ions is about 100 times smaller than this.

In the flame away from the electrodes the electric force is found to be proportional to the current, so that here the flame obeys Ohm's law like a metallic conductor. Its conductivity is about 10¹¹ times less than that of copper. In the equation $V = Ai^2 + Bdi$, the term Bdi is the part of the E.M.F. used up between the electrodes, so it is proportional to the current and to the distance. Prof. Sir J. J. Thomson has shown theoretically that the drop of potential near the electrodes should be proportional to the square of the current, as is found experimentally to be the case.

The conductivity of a Bunsen flame may be compared with the conductivity of liquids, such as water. In pure water some of the molecules are dissociated into ions and the water is a conductor, although only a poor one. But if a salt like sodium chloride is dissolved in the water the salt dissociates into ions almost completely, and the con-

ductivity is greatly increased. Suppose we hold a bead of salt on a platinum wire in a flame, then the salt volatilises and the flame is filled with its vapour, and, just as with the water, the conductivity is enormously increased.

With the long flame and an electrode at each end, we can try the effect on the current of putting salt in different parts of the flame between the electrodes. In this way it is easy to show that the current is practically unchanged, unless the salt vapour is put in close to the negative electrode, but in that case it produces a very great increase in the current. This confirms the conclusion that nearly all the resistance to the passage of the current is situated close to the negative electrode. When the salt is put in anywhere it diminishes the resistance there to a small fraction of its value, but it is only close to the negative electrode that the diminution in the total resistance is appreciable. If we measure the potential difference between two points in the flame away from the electrodes, and then put salt vapour in the flame between them, we find that the P.D. drops to a small fraction of its value although the current is the same as before. This shows clearly that the salt vapour greatly increases the conductivity wherever it is put in.

If some salt is put on the negative electrode, the sudden drop in potential there almost disappears, and we get a nearly uniform potential gradient from one electrode to the other, so that now the resistance is nearly uniformly distributed along the flame. If now salt vapour is put in anywhere between the electrodes the current is increased. If, for example, we fill half the length of the flame with salt vapour, we nearly double the current.

When salt is put on one electrode, the flame can be used as a rectifier for an alternating current, for when the salted electrode is negative the resistance of the flame is much smaller than when it is positive.

I have measured the conductivities of a number of alkali salt vapours in a current of air flowing along a platinum tube heated in a gas furnace. An electrode was fixed along the axis of the tube, and the current from it through the salt vapour to the surrounding tube was measured with a galvanometer. It was found that at temperatures above 1400° C., and with electro-motive forces of about 1000 volts, the current was proportional to the amount of salt passing through the tube, and for different salts in equal quantities inversely proportional to the electro-chemical equivalent of the salt. This shows that the quantity of electricity per molecule of salt is the same for all salts. It was also found that the quantity of electricity carried per molecule was equal to that carried per molecule when a solution of salt in water is electrolysed. It appears therefore that the laws of electrolysis discovered by Faraday for liquids apply also to salts in the state of vapour.

When a molecule of salt like sodium chloride dissociates into two ions in water, the sodium atom forms the positive ion and the chlorine atom the negative ion, and when a current is passed through the solution the sodium is attracted to the negative electrode and the chlorine goes to the positive electrode. We might expect the same thing to happen when a current is passed through the salt vapour in a flame. If we put two wires in the flame, and put some sodium salt on one and then connect them to an induction coil, and pass a discharge from the salted one to the other, we find that the yellow sodium vapour appears at it when it is the negative pole but not when it is positive. This shows that in the flame the positive ions of the salt vapour contain the metal just as they do in solutions. The negative ions, however, do not appear to be the same in flames as in solutions. In flames the very high velocity of the negative ions indicates that they are the electrons whose properties have been investigated in vacuum tubes by Sir William Crookes and Sir Joseph Thomson. The positive ion, then, is an atom or molecule, while the negative ion is an electron, the mass of which is several thousand times smaller. This is the explanation of the fact that the negative ions move 100 times more quickly than the positive ions.

A METHOD FOR PREPARING STANDARD HYDROCHLORIC ACID SOLUTIONS.

By G. A. HULETT and W. D. BONNER.

WE find that the "constant boiling" hydrochloric acid has a very definite percentage composition, is easily obtained, and from it a standard solution of hydrochloric acid may be made directly and with ease and accuracy. In some of the older text-books on quantitative analysis it is recommended that a constant boiling hydrochloric acid be used to make approximate solutions and then standardised, but we have found no notice of its being used as a basis for volumetric work.

It has long been known that hydrochloric acid, when distilled, will approach a point where it distils over unchanged in composition whether we start with a strong or weak acid in the still, and when this point is reached the residue in the still has the same composition as the distillate. We are concerned with the definiteness of the composition of the constant boiling acid and its variation with the pressure. The last point will be considered first, as the work of Roscoe and Dittmar gave sufficient data on this point (*Journ. Chem. Soc.*, 1860, 128; and Roscoe, *Ann.*, cxvi., 343). These investigators determined the composition of the constant boiling hydrochloric acid obtained when distilling under pressures varying from 65 mm. to 2510 mm., and on plotting these results on a large scale it was found that a satisfactory curve could be drawn, and it appeared that for the region with which we are concerned (660 to 860 mm.) that a change of 10 mm. in pressure produced a change of only 0.024 per cent in the composition of the acid. For this region the acid obtained is about 20 per cent hydrochloric acid, and a change of 10 mm. in the barometric pressure caused a change of only one part in 4000, so it would seem that only for the most exact work need the barometric pressure be considered when preparing the constant boiling hydrochloric acid, but we have given below the exact values for the different pressures.

Information on the composition and reproducibility of the constant boiling acid was obtained by experiment. Samples of commercial "chemically pure" hydrochloric acid were diluted to various strengths and distilled from an ordinary distilling flask provided with a Liebig condenser. The distillate was rejected until the temperature was constant, and then samples were taken at intervals and titrated as well as a sample of the residue. A number of experiments showed that it was necessary to distil over three-fifths of the acid taken before the constant boiling acid was obtained.

A one-twentieth degree Beckmann thermometer was used, and was carefully calibrated for the boiling-point of water at 760 mm. This temperature of 100.00° was 10.12 on the scale, and it was possible to read to 1/100° with this thermometer, and the scale had been calibrated for this range of temperature. Starting with an acid of $d = 1.117$, the constant boiling reading was 18.40 with the barometer at 763.7, and this gave 108.53° as the observed temperature after all corrections had been made. A second experiment, starting with an acid $d = 1.131$, gave as the constant boiling-point 108.55°. These experiments gave us an accurate determination of the constant boiling temperature of mixtures of hydrochloric acid and water (108.54° at 763 mm.)—but showed that unless elaborate precautions were taken that this was not a reliable guide for the constant boiling acid. We have found, however, that when starting with an acid anywhere in the range of densities from 1.09 to 1.15 and distilling over 75 per cent the remaining distillate and residue were well within the constant boiling region, as the problem was, from the practical side, a very simple one.

In determining the composition of the distillates and residues it was found that titration with a standard alkali did not give the desired accuracy, the conductivity of hydrochloric acids of this strength changed only slightly

with the composition, but it appeared from tables of densities of hydrogen chloride solutions, that in the vicinity of 20 per cent a change of 0.00001 in the density made a change of only 0.002 per cent in the composition, and this accuracy was attainable with the Ostwald-Sprengel pycnometer used. A constant temperature-bath was maintained at 25.00°, within one-fiftieth degree, and this was the temperature of all the determinations. A uniform method of drying and weighing the pycnometer was employed and all observations were corrected to vacuum weights, so the densities (d_{25}) represent the ratio of mass to volume at 25°.

It was hardly expected that evaporation on an ordinary water-bath would give a definite residue, but two experiments were made.

500 cc. $d = 1.114$ evaporated to 152 cc. P 746 d_{25} of residue = 1.10625.

500 cc. $d = 1.078$ evaporated to 137 cc. P. 746 d_{25} of residue = 1.10479.

The results are high and the agreement is not better than 0.3 per cent. This is probably due to the fact that air had access to the surface of the evaporating liquid, producing the same effect as distilling under a diminished pressure—which was variable.

An experiment was made by boiling acids in ordinary beakers over a free flame—

500 cc. $d = 1.114$ boiled down to 162 cc. P 762.5 d_{25} of the residue = 1.09816.

500 cc. $d = 1.078$ boiled down to 137 cc. P 762.5 d_{25} of the residue = 1.09775.

Here the difference in composition of the residue is less, being only about 0.08 per cent, but they are both higher than the constant boiling acid by some 0.4 per cent, so it would seem that boiling in a beaker does not prevent the air from penetrating to the surface of the boiling liquid and producing the effect of boiling under diminished pressure (which increases the percentage of acid). We have not found an effect due to superheating, for the presence or absence of platinum tetrahedrons made no measurable difference in the composition of the constant boiling acid, but it was evident from the preceding experiments that it was quite essential to enclose the acid in a flask where the air was completely removed by the vapour, and it was certain that acid was finally boiling in contact with its vapour alone and at the observed barometric pressure.

750 cc. of concentrated acid were distilled and 500 cc. of the distillate with density 1.158 were re-distilled with the barometer at 758.5. The first 100 cc. of the distillate were rejected and the densities of the following portions were taken.

100—120	$d_{25} = 1.1188$
110—120	$d_{25} = 1.1001$
240—260	$d_{25} = 1.0975$
360—380	$d_{25} = 1.09625$
Residue	$d_{25} = 1.09615$

Here the portion 360—380 cc., counting from the beginning, and the residue differ by only 0.02 per cent of hydrochloric acid. The exact composition will be given later. 1260 cc. of acid $d = 1.103$ were distilled at 760.0, after 900 cc. had been distilled over the following 2.10 cc. and the residue of 150 cc. were examined with the following results:—

900—1110 distillate	$d_{25} = 1.09615$
Residue	$d_{25} = 1.09625$

900 cc. $d = 1.106$ were distilled at 755.6 mm. and 740 cc. of the distillate rejected; the following 140 cc. showed $d_{25} = 1.09621$, the residue was lost.

1000 cc. acid $d = 1.089$ were distilled at 762 mm. until 840 had distilled over—and the following 130 cc. showed $d_{25} = 1.09612$. The residue of 840—970, only 30 cc., was not examined. It must be borne in mind that the residue will contain all the non-volatile impurities and chlorides the acid has collected, so the density of the residue, or analysis as silver chloride, would be open to question, unless the

acid had been re-distilled, but the distillate is free from this source of error and we have found that ordinary commercial "muriatic acid" will give reliable results.

A determination of the composition of the constant boiling acids obtained was made by the silver chloride method. After making the density determinations the content of the pycnometer was washed into a litre flask and diluted to the mark. Samples of 50 cc. were taken for analysis and the silver determined as silver chloride with the aid of a Gooch crucible, taking the usual precautions. The flask and pipette were calibrated to hold a volume at 20° and the temperature was controlled, and thus the silver chloride weighed represented the chlorine in one-twentieth of the weight of the acid in the pycnometer or for 3.5694 grms. (air weight) of the constant boiling distillate, and the results of these analyses are given in the last column of the following table:—

	D ₂₅ of distillate.	P.	D ₂₅ cal. for 760 mm.	AgCl from 1.5694 grms. of the distillate.
1.	1.09625	758.5	1.09624	—
2.	1.09615	760.0	1.09615	a 1.2491 b 1.2480
3.	1.09612	762.0	1.09615	a 1.2473 b 1.2469
4.	1.09621	755.6	1.09625	a 1.24863 b 1.24857

From these results we take the density of the constant boiling distillate at 760 mm. to be $d_{25} = 1.09620$ and 1.5694 grms. air weight of this distillate equivalent to 1.2486 grms. AgCl. Taking silver to be 107.88, chlorine 35.46, and hydrogen 1.008 we have for silver chloride 143.34, and for hydrochloric acid 36.47. On this basis a molecular weight of silver chloride would require 180.170 grms. (air weight) of the constant boiling acid, and this weight would contain one molecule (36.47 grms.) of HCl or 20.240 per cent.

By starting with hydrochloric acid about $d = 1.10$, made up with an ordinary hydrometer or specific gravity balance, and distilling off three-fourths of the liquid taken, the following distillate should not differ by more than one part in 10,000 from the figures given in the following table. This constant boiling acid is not hygroscopic or noticeably volatile and may be easily weighed in a little flask. By using a capillary pipette joined to a piece of flexible rubber tubing, to adjust the last amount of acid, it is a very simple matter to weigh out 180.170 grms. to less than 10 mgrms., and this will give a normal solution with an accuracy that is seldom attained even with very elaborate precautions.

164.42 cc. of this constant boiling acid (at 25°) contains a molecule of hydrochloric acid and one cubic centimetre contains 6.08 millimols of hydrochloric acid, figures which may be of use in making up solutions, but volume measurements are less accurate than weight determinations, while the latter are free from variations with the temperature. Only for the most accurate work need one consider the pressure under which the acid is distilled if the barometer is in the vicinity of 760, but we have calculated the following tables from the results obtained in this work and the values given by Roscoe and Dittmar.

Pressure.	Per cent HCl.	Grms. constant boiling distillate for 1 mol. HCl.
770	20.218	180.390
760	20.242	180.170
750	20.266	179.960
740	20.290	179.745
730	20.314	179.530

Both sulphuric and nitric acids give constant boiling mixtures but seem to be less desirable in several particulars than hydrochloric acid, which may serve as a reference basis, directly or indirectly, for most solutions.

We have found: That the temperature of the constant boiling hydrochloric acid is 108.54° at 763 mm. pressure.

That the density of the constant boiling distillate at 760 is $d_{25} = 1.09620$, and that it contains 20.242 per cent of hydrochloric acid.—*Journal of the American Chemical Society*, xxxi., No. 3.

THE QUANTITATIVE PRECIPITATION OF TELLURIUM DIOXIDE AND ITS APPLICATION TO THE SEPARATION OF TELLURIUM FROM SELENIUM.

By PHILIP E. BROWNING and WILLIAM R. FLINT.

ALL those processes for the estimation of tellurium in which the tellurium is precipitated and weighed in elementary condition are open to the objections that, first, there is more or less difficulty in securing completeness of precipitation owing to the rapid increase of free acid in the solution (Crane, *Am. Chem. Journ.*, xxiii., 409; see also Lenher and Homburger, *Journ. Am. Chem. Soc.*, xxx., 387); and, second, the product is extremely susceptible to oxidation. On the other hand, those methods in which compounds decomposable by heat are transformed to the dioxide by ignition are generally both tedious by reason of the length of time required (as, for example, the basic nitrate process as described by Norris, *Journ. Am. Chem. Soc.*, xxviii., 1675), and, what is more to the point, liable to errors caused not only by lack of constancy of composition, but also by the volatilisation of the product to be weighed.

Of all the forms in which tellurium has been weighed there is no doubt that the dioxide is the best. It is unaffected by the air, is anhydrous, is not hygroscopic, and can easily be obtained in pure condition. Likewise it can be heated to any temperature below low redness without any danger of volatilisation. It was in view of these facts that some results obtained from an extensive study, about to be published, of the hydrolytic behaviour of hydrochloric acid solutions of tellurium tetrachloride suggested the process about to be described.

When a tetrachloride solution containing the least possible excess of hydrochloric acid is sufficiently diluted with hot water, but a small portion, if any, of the tellurium is at first precipitated. By the addition of as little ammonia in excess as may be, and the restoration of the acidity by acetic acid in the faintest possible excess and then allowing the liquid to stand until cold, the tellurium is precipitated completely, as TeO₂, but in very finely crystalline condition. The precipitate is insoluble in cold water and alcohol, in acetic acid and ammonium acetate solutions of one per cent strength if cold, and filters, washes, and dries with the greatest facility.

In the first testing of the method, portions of pure dioxide were weighed out, dissolved in two cubic centimetres of concentrated hydrochloric acid, diluted with two hundred cubic centimetres of boiling water, and the ammonia, and subsequently acetic acid, added with great care. After standing over night, the liquid was decanted through the asbestos of a Gooch crucible, and the precipitate transferred and washed with cold water, and dried to constant weight at about 105°. In Table I., experiments 1 to 4, are gathered the results obtained.

TABLE I.

	TeO ₂ taken. Grm.	TeO ₂ found. Grm.	Error. Grm.
1.	0.2002	0.2000	—0.0002
2.	0.2019	0.2017	—0.0002
3.	0.2004	0.2002	—0.0002
4.	0.2006	0.2004	—0.0002
5.	0.2011	0.2010	—0.0001
6.	0.2003	0.2003	—

In experiments 5 and 6, one and one-half cubic centimetres of ten per cent potassium hydroxide solution were used to dissolve the dioxide, instead of hydrochloric acid. The solution was then acidified slightly with hydrochloric acid, and the determinations completed from this point as before. The results seem to be equally good.

Next, weighed amounts of basic nitrate were dissolved in two cubic centimetres of hydrochloric acid. The small

quantity of nitric acid holds up a little of the tellurium (Gutbier, "Studien über das Tellur," 46) and consequently before dilution resort was had to evaporation to remove as much of the free acid as possible. This had to be done with extreme care, since the least tendency on the part of the solution to boil was accompanied by the volatilisation of the tetrachloride formed. With a not unreasonable amount of care, however, good results were obtained. In all of the experiments of Table II. the dilution was with hot water, two hundred cubic centimetres being sufficient, but in several the treatment was varied, as given below:—

TABLE II.

	$2\text{TeO}_2\cdot\text{HNO}_3$ taken.	TeO_2 theory.	TeO_2 found.	Error.
	Grm.	Grm.	Grm.	Grm.
1.	0.2508	0.2094	0.2079	-0.0015
2.	0.2501	0.2088	0.2086	-0.0002
3.	0.2521	0.2105	0.2101	-0.0004
4.	0.2500	0.2088	Not completed	
5.	0.2537	0.2118	0.2115	0.0003
6.	0.2510	0.2096	0.2091	-0.0005

In experiment 1, during the evaporation of the acid, there was noticed a slight volatilisation of the tetrachloride, which accounts for the increased error. In 2, filtration was performed after twelve hours, and the same length of time elapsed in 5 and 6. Experiment 3 stood for two hours, and in this and number 4 potassium hydroxide was used in place of ammonia. So much tellurium was found in the filtrate from 4 that the determination was not completed. In 5 and 6 the basic nitrate was dissolved with two cubic centimetres of ten per cent potassium hydroxide solution, instead of the usual hydrochloric acid. Before dilution with hot water, hydrochloric acid was added in very slight excess. The ammonia added in number 6 was so much in excess as to dissolve completely the precipitate formed. The increased amount of ammonium acetate produced in the solution probably held up a trace of tellurium.

In order to observe the effects produced by variations in the factors concerned in the process, several experiments were performed, the figures for which are given in Table III.

TABLE III.

	$2\text{TeO}_2\cdot\text{HNO}_3$ taken.	TeO_2 theory (Te taken as 127.5).	TeO_2 found.	Error.
	Grm.	Grm.	Grm.	Grm.
1.	0.2502	0.2089	0.2083	-0.0006
2.	0.2524	0.2108	0.2110	+0.0002
3.	0.2505	0.2092	0.2089	-0.0003
4.	0.2528	0.2111	0.2106	-0.0005
5.	0.2531	0.2113	0.2106	-0.0007
6.	0.5008	0.4182	0.4182	—
7.	0.5010	0.4183	0.4175	0.0008
8.	0.5005	0.4179	0.4178	-0.0001

The first four and the eighth were allowed to stand over night before the precipitate was removed; in the fifth one quarter hour, and in the sixth and seventh one half hour, elapsed. By a comparison of the results it appears that very little difference is made whether the time allowed to elapse be from fifteen to thirty minutes or twelve or more hours, so long as the liquid is thoroughly cooled.

In all of the experiments of this series the basic nitrate was dissolved with ten per cent potassium hydroxide solution, two cubic centimetres being sufficient in the first five and four in the last three numbers. The solution in the case of the first two was then acidified slightly with hydrochloric acid, before dilution with hot water. In the rest, the alkaline solution was simply diluted with boiling water and faintly acidified with acetic acid, the precipitate being afterwards made crystalline by further heating (Berzelius, *Ann. der Chim. et de Phys.*, 2 serie, lviii., 134). It was noted that the precipitate formed by this variation of the method is not so quickly transformed to the crystalline condition as when the procedure of the experiments described in Table I. is followed. It is,

besides, still more finely divided and does not settle quite so well. There seems to be a distinct advantage in the use of ammonia, when added to the solution acidified with hydrochloric acid, since, if the diluted solution is sufficiently hot, the precipitate formed by the ammonia begins to become crystalline, apparently, at about the time when the point of neutrality is reached. Under these conditions, a few drops of dilute ammonia in excess have an inappreciable solvent effect upon the TeO_2 , and consequently there is also no opportunity for the slight excess of acetic acid subsequently introduced to dissolve and thus hold up a trace of the tellurium. On the other hand, it seems probable that, when the acetic acid is introduced, in faint excess, into the hot diluted solution, alkaline with potassium hydroxide, since the tellurium is precipitated in floccy form which does not become entirely crystalline until again heated, the excess of acid must dissolve up a more or less minute portion of the precipitate and retain it in solution in such a form as not to be again thrown down upon cooling. Two facts may be adduced in support of this theory, namely, first, that the errors in Table III. show much greater irregularity than those of Table I.; and second, that whereas the filtrates of I. were shown by testing with stannous chloride to be free from tellurium, several of those in II., notably experiments 4, 5, and 7, were proved to contain it in traces.

And, finally, the last three experiments of Table III. show that it is perfectly possible to use quite as successfully one-half grm. of the basic nitrate, equivalent to four-tenths grm. of dioxide, in a single determination, employing a bulk of solution no greater than 200 to 250 cubic centimetres.

Attempts to separate tellurium from copper and bismuth by treatment with small amounts of potassium hydroxide solution, and to estimate the tellurium in the filtrate by this ammonia-acetic acid process, met with only moderate success. Under the conditions, the copper and bismuth apparently tend to form insoluble tellurites undecomposable by the allowable excess of alkali (*Ibid.*, lviii., 114), and consequently there was always a loss of tellurium. And, further, if the bismuth or copper is precipitated together with the tellurium, it is practically impossible to dissolve out from the mixed precipitate all the tellurium by a hot solution of the alkali. The results of two experiments with mixtures of bismuth and tellurium oxides are given in Table IV.

TABLE IV.

	TeO_2 taken.	Bi_2O_3 taken.	TeO_2 found.	Error.
	Grm.	Grm.	Grm.	Grm.
1.	0.2027	0.005	0.2015	-0.0012
2.	0.2009	0.005	0.1997	-0.0012

In both cases the mixed oxides were heated with two cubic centimetres of potassium hydroxide solution (10 per cent), the precipitate filtered out, and the filtrate diluted with hot water and precipitated by addition of acetic acid.

If hydrochloric acid solutions of tellurium and selenium dioxides be mixed, abundantly diluted with boiling hot water, and the operation of the above described process properly applied, only the tellurium is precipitated, the selenium remaining entirely in solution in the filtrate. This not only provides a simple and rapid preparative process for the purification of tellurium from selenium, but also makes possible the estimation of tellurium directly in the presence of the latter element.

TABLE V.

	TeO_2 taken.	SeO_2 taken.	TeO_2 found.	Error.
	Grm.	Grm.	Grm.	Grm.
1.	0.2015	0.2	0.2010	-0.0005
2.	0.2013	0.1	0.1996	-0.0017
3.	0.2003	0.1	0.1992	-0.0011
4.	0.2009	0.1	0.2003	-0.0006
5.	0.2000	0.1	0.2002	+0.0002
6.	0.2015	0.1	0.2016	+0.0001
7.	0.2038	0.1	0.2040	+0.0002
8.	0.2028	0.05	0.2019	-0.0009
9.	0.2024	0.05	0.2024	—

Experiment 1 in Table V. was made upon 0.2 gm. of TeO_2 in the presence of 0.2 gm. of SeO_3 , which was later found to contain a little copper. After solution of the oxides in two cubic centimetres of hydrochloric acid, and dilution to 200 cubic centimetres with hot water, precipitation was effected as usual by ammonia and acetic acid. Copper was carried down in the precipitate, as shown by its greenish colour, the total weight after thorough drying being 0.2054 gm. In order to determine the amount of TeO_2 per cent the precipitate was washed with ten per cent potassium hydroxide solution, the tellurium being carried away in solution as tellurite; the residue was washed with water until free from soluble matter, and dried to constant weight, yielding 0.0044 gm. The amount of TeO_2 by difference was consequently 0.2010 gm. But the residue, when dissolved in hydrochloric acid and tested with stannous chloride, showed the presence of a trace of tellurium.

In experiment 2, two cubic centimetres of the potassium hydroxide solution were used, and the hot diluted solution acidified with acetic acid. In 3 and 4, after the solution in two cubic centimetres of potassium hydroxide, hydrochloric acid was added in faint excess, and the hot diluted solution treated with ammonia and then acetic acid; the difference between these two determinations is apparently explained by the fact that in experiment 3 the solution was allowed to cool a little before addition of ammonia, and thus the floccy precipitate was attacked by the acetic acid. In experiments 5, 6, and 7, potassium hydroxide was used to dissolve the oxides, hydrochloric acid was added to faint acidity, and the dilution made with cold water, which was then heated to boiling. It was evident that the floccy precipitation caused by the cold water included some selenium, which was not released by the change to crystalline form, since not only are the errors positive, but also the precipitate, when tested for selenium with potassium iodide by the delicate method of Norris, Fay, and Edgerly (*Am. Chem. Journ.*, xxxiii., 105), showed the presence of a trace of that element. In order to be certain that this is the true explanation of the fact, two more experiments, 8 and 9, were performed, in the first of which special care was taken to dilute with water actively boiling, and to carry out the subsequent operations as quickly as possible in order that the change of condition of the precipitate might occur before the acetic acid was introduced. No selenium could be detected in the precipitate of experiment 8. In the case of 9, the hot solution was allowed to cool somewhat before the precipitation, in consequence of which the abundant floccy precipitate included a minute trace of selenium, as afterwards proved by the above mentioned test.

In order, therefore, to estimate tellurium as the dioxide by this method, it is evident that fairly accurate and concordant results can be obtained by dissolving the material in ten per cent potassium hydroxide solution, about two cubic centimetres for 0.2 gm. of dioxide, acidifying this solution slightly with hydrochloric acid, diluting to 200 cubic centimetres with boiling hot water, and precipitating the tellurium in a finely crystalline form of dioxide from the still hot solution by the careful addition of dilute ammonia in faint excess and the restoration of the acidity by the faintest possible excess of acetic acid. If these simple operations are properly carried out, the precipitate will have become crystalline by the time when the excess of ammonia has been reached; the addition of a few drops of acetic acid will cause the precipitation to become entirely quantitative when the solution has cooled, so that no tellurium will be detectable in the filtrate by stannous chloride; the precipitate can be transferred, and safely and rapidly washed with cold water, and dried to constant weight at about 105° (or even up to just below low redness) in a quarter of an hour. Furthermore, the filtration can be performed at the end of half an hour or so, or after twelve to twenty-four hours, as most convenient. And, as shown by the experiments of Table V., selenium does not interfere, providing precautions are taken.—*American Journal of Science*, xxviii., p. 112.

NOTICES OF BOOKS.

Exercises in Physical Chemistry. By Dr. W. A. ROTH. Authorised Translation by A. T. CAMERON, M.A., B.Sc. London: Archibald Constable and Co., Ltd. 1909.

THE requirements of the student who is beginning physical chemistry are well met in this book, which contains clear directions for a practical course in the subject, involving the use of no apparatus which is not to be found in any reasonably well equipped laboratory. The methods of carrying out determinations are described explicitly, and suggestions are made for additional exercises. Theory and practice are well blended, and each chapter will repay carefully reading in the study before the practical work is begun. Although the theoretical parts will probably require supplementing either by lectures or further reading they are complete as far as they go, and the most important features of each subject are emphasised. The first part includes the determination of molecular weights and optical constants and also thermochemical determinations, and the translator has added a chapter on the construction and use of the thermostat. The fundamental principles and experiments of electrochemistry are well described in the second part, in which the author has been judicious in choosing his experiments, and has taken care not to ascribe to his readers an extensive knowledge of physics, which is not infrequently done in books on electrochemistry.

Cane-sugar and its Manufacture. By H. C. PRINSEN GEERLIGS. Altrincham: Norman Rodger. 1909.

THIS book is a compendium of the chemistry of the manufacture of sugar and contains many tables of statistics and numerical data obtained during the course of the author's work in Java at the head of the West Java Sugar Experiment Station. In the first part, which deals with the constituents of sugar, the properties and derivatives of glucose and fructose are considered in detail, and the proportions of these and other constituents of the sugar-cane are tabulated, many details being given as to the distribution of the constituents at different periods of the growth of the plant and in different parts of the stalk. The second part gives an account of the manufacture of sugar, and each step of the process is followed in detail with explanations of its chemistry and technology. The engineering side of the subject and information relating to machinery are not regarded as coming within the scope of the book, and the treatment is on the whole more scientific than practical, or rather the scientific side of practical questions is specially discussed. The manufacturer as well as the chemist will, however, find the book of value, for such points as the preservation of sugar during storage and transport are discussed, and hints are given as to the best methods of overcoming difficulties in the way of keeping sugars in good condition.

Report of the Eleventh Meeting of the Australasian Association for the Advancement of Science held at Adelaide, 1907. Edited by WALTER HOWCHIN, F.G.S. Adelaide: Published by the Association.

THE report of the Eleventh Meeting of the Australasian Association for the Advancement of Science contains the addresses of the Presidents of the sections and also the Proceedings of each section. Some of the more important papers are printed in full, and abstracts of others have been prepared. The papers show how vigorous has been the growth of this comparatively young society, and the valuable work which has been done by it in promoting scientific research in Australia. As might be expected the papers on anthropology are particularly interesting, and the inaugural address delivered by the President on Personal Reminiscences of Central Australia contains a graphic account of the Burke and Wills expedition to the interior and the reasons for its failure.

Laboratory Methods of Inorganic Chemistry. By HEINRICH BILTZ and WILHELM BILTZ. Authorised Translation by WILLIAM T. HALL and ARTHUR A. BLANCHARD. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1909.

THE arrangement of the material in this book is rather different from that usually adopted in laboratory manuals, and the advantage certainly seems on the side of the authors' method, which is somewhat allied to that advocated in very early text-books of chemistry. One of the first tasks of the student who is beginning a college course after his school work in chemistry is very often the study of general methods of preparation of classes of compounds, thus linking up the knowledge of the isolated derivatives of each element. Thus, while he is actually learning no new facts, he is grasping how what he has already learnt fits into a rational scientific scheme. This laboratory book, then, provides him with suitable practical work to accompany and illustrate this task of generalisation. After an introductory chapter dealing with general methods and operations it treats of the preparation of the elements, and then passes to the binary compounds and thence to more complex derivatives. All details as to amount of material, yield, &c., are given in full, and as the book is intended for the use of fairly advanced students, methods of preparation in various states—colloidal and amorphous, for example—are included in a very useful chapter. Some complicated compounds are described, such as the ammonia-cobaltic compounds, and it is at least doubtful whether this is quite judicious, for the student who is sufficiently advanced to profit by the preparations should also be able to follow the accounts given in the original papers, the reading of which would probably benefit him in more ways than one, and even if he took a little longer over them it would be time well spent. The preparation of some esters and organo metallic substances as well as the compounds of the rare earths is included in the book, which gives a valuable course of synthetic inorganic chemistry. It must be mentioned that the translation contains the authors' additions and alterations which are to be made in the second German addition.

Colloids and the Ultramicroscope. By Dr. RICHARD ZSIGMONDY. Authorised Translation by JEROME ALEXANDER, M.Sc. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1909.

THIS is a book which may without exaggeration be described as epoch making, and all workers in the region of colloid chemistry who do not already possess the German edition will be well advised to get the translation into English. It contains a detailed account of the author's own investigations on colloids and of the perfection of the ultramicroscopic method, and also includes a short review of the publications of other workers in the same field. A clear summary is given of the results which have so far been obtained, and it requires but little penetration to see that they must be followed by important practical developments in almost every branch of applied chemistry. Two beautiful coloured plates have been added to the English edition, showing the subdivisions of gold in order of increasing size of the particles in incident and transmitted light respectively. The translation has had the advantage of revision by the author himself, who has not only seen that the meaning of the original is faithfully reproduced, but has also made some additions to the text necessitated by the publication of recent work.

Grundriss der Kolloidchemie. ("Outlines of Colloid Chemistry"). By Dr. W. OSTWALD. Dresden: Theodor Steinkopff. 1909.

THE time is quite ripe for the appearance of a complete treatise on colloid chemistry in which a certain amount of judicious selecting of material has been performed, and the almost countless results of different workers have been co-ordinated so that any particular branch or aspect of the

subject can be looked up without reference to periodicals or original articles. This book contains a complete survey of the whole region of colloid chemistry, showing its phenomena and the laws governing them, and the history of the subject from the time of Graham's first researches to the present day is included. The large number of theoretical conceptions which have been put forward the author has not attempted to reproduce exhaustively, but has rather endeavoured to pick out those theories which appear to him to explain most simply and satisfactorily the greatest number of phenomena and to discuss and criticise them fully. The author has shown a considerable amount of skill in marshalling the facts which the investigations of the phenomena of colloid chemistry have brought to light, and the arrangement of the text is thoroughly systematic.

Gewinnung und Reinigung des Kochsalzes. ("Preparation and Purification of Common Salt"). By Dr. CARL RIEMANN. Halle-a-S.: Wilhelm Knapp. 1909.

THIS short monograph, which is Volume xvii. of the Series of Monographs on Technical Chemical Manufactures, gives an outline of methods of obtaining and purifying salt, and although it merely touches upon many important points it will serve its purpose as an introduction to larger works. The origin of the salt deposits of the earth's crust is discussed fairly fully, and the different methods of mining it and freeing it from impurities are illustrated. Naturally English practice is not treated so fully as methods in use upon the Continent, which limits the usefulness of the book in this country; in addition, it presents the very serious disadvantage of having no alphabetical index.

Fahrbuch der Elektrochemie und Angewandten Physikalischen Chemie. ("Year Book of Electrochemistry and Applied Physical Chemistry"). Edited by Dr. phil. HEINRICH DANNEEL. Twelfth Year. Halle-a-S.: Wilhelm Knapp. 1909.

ALTHOUGH this Annual is somewhat late in appearance this fault will perhaps be condoned in view of its completeness. Every recent development in electrochemistry is carefully chronicled and full references are given, so that additional details can readily be looked up in the original papers. The volume, like its predecessors, contains a review of recent books dealing with electrochemistry; this survey gives some indication of the scope and character of every book of importance which was published during 1905. Both pure and applied electrochemistry are considered, and information is given relating to improvements in apparatus and machinery, and also to theoretical developments up to the end of the year 1905.

Verhalten der Wichtigsten Seltenen Erden zu Reagentien. ("The Behaviour of the most Important Rare Earths towards Reagents"). By Dr. JOS. v. PANAYEFF. Halle-a-S.: Wilhelm Knapp. 1909.

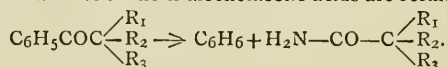
THE rare earths treated in this monograph include zirconium, thorium, cerium, didymium, lanthanum, yttrium, and erbium, of which both the dry and wet reactions are given. It will be seen from the list that there are some notable omissions, but, on the other hand, such elements as are included are dealt with thoroughly, the results obtained with more than twenty reagents, both inorganic and organic, being stated for each. A short preface is given to each substance dealing with its occurrence and chemistry and the properties of the more important salts. No separation tables are included, but they could easily be constructed from the information in the text. The book is more than a mere compilation, the results of the author's own research work on the rare earths being incorporated in it, and it will be found that there are many observations which differ from those of other workers and which will require testing before they are accepted. The reactions of praseodymium and neodymium are given together under the name didymium, although the properties of the two elements are treated separately.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlix., No. 1, July 5, 1909.

New Triacetalacetophenones and Triacetalacetic Acids derived from them.—A. Haller and Edouard Bauer.—The authors' researches have shown that by means of sodamide alcoholic radicals can be substituted for the hydrogen of acetophenone, and, moreover, whatever these radicals are, the decomposition of the triacetalic ketone by means of sodamide always takes place in such a way that the amides of the triacetalacetic acids are formed:—

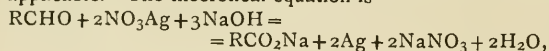


Among compounds prepared thus may be mentioned the amide of benzylidimethylacetic acid.

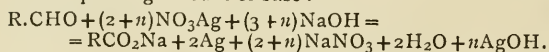
Radio-activity of Salts of Potassium.—Emile Henriot and G. Yavon.—The examination of the chloride and sulphate of potassium by the electrical method confirms the hypothesis that the radio-activity of potassium is due to the element itself and not to an unknown impurity. The rays possess the penetration of β -rays, and, moreover, in a magnetic field they behave like a flow of negative electricity, and hence there is no doubt that they are β -rays.

Chlorides of Silicon.—A. Besson and L. Fournier.—When the recently discovered compounds SiH_2Cl_2 and SiH_3Cl are exposed to the action of the dark discharge, after having been previously condensed, brown or yellow residues are obtained which have the formulae Si_2Cl_3 and Si_2Cl_4 , and which appear to be unsaturated chlorides. The chlorides of the saturated series can also be prepared by subjecting a mixture of dry hydrogen and SiCl_4 vapour to the discharge. There is a limit to this reaction, for even if an excess of hydrogen is employed a fairly large proportion of SiCl_4 remains unchanged. By this method the authors have isolated $\text{Si}_4\text{Cl}_{10}$ and $\text{Si}_5\text{Cl}_{12}$.

Oxidation of Aldehydes by Silver Oxide.—Marcel Delépine and Pierre Bonnet.—By adding soda to a mixture of silver nitrate and aldehyde the latter can be oxidised very readily in the cold, and this method is very generally applicable. The theoretical equation is—



but it is often better to use an excess of silver nitrate with a corresponding amount of base:—



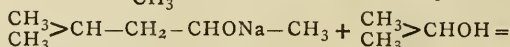
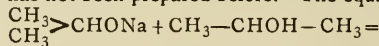
It is quite unnecessary to prepare the silver oxide beforehand, and the presence of silver nitrate does not in any way hinder the oxidation.

No. 2, July 12, 1909.

Neutral Carbonates of Rubidium and Cæsium.—M. de Forcrand.—From determinations of the heats of solution of the carbonates of rubidium and cæsium, it appears that rubidium carbonate resembles potassium carbonate as far as the degree of hydration is concerned ($1.5\text{H}_2\text{O}$), while cæsium carbonate differs from them ($3.5\text{H}_2\text{O}$). Thus the formulae are $2\text{M}_2\text{CO}_3 + 3\text{H}_2\text{O}$ for K_2 and Rb_2 and $2\text{Cs}_2\text{CO}_3 + 7\text{H}_2\text{O}$. The results obtained when the hydrates of Rb_2CO_3 and Cs_2CO_3 are subjected to the action of heat seem to show that there are several hydrates between the monohydrate and the anhydrous salt, corresponding to different degrees of condensation of the molecule, but the author has not isolated these compounds. The anhydrous carbonates are powerful dehydrating agents, being even more active than anhydrous K_2CO_3 .

Chemical Action of the Penetrating Radium Rays on Water.—Miroslaw Kernbaum.—The author has determined quantitatively the amount of hydrogen peroxide formed by the action of the penetrating radium rays on water, and concludes that the equation expressing the reaction is $2\text{H}_2\text{O} = \text{H}_2\text{O}_2 + \text{H}_2$. It is probable that the action is due to the β -rays, and that the γ -rays do not take any part in it.

Condensation of Isopropyl Alcohol with its Sodium Derivative.—Marcel Guerbet.—When isopropyl alcohol, $\text{C}_3\text{H}_8\text{O}$, is heated to 200° with its sodium derivative, the condensed alcohols methylisobutyl carbinol, $\text{C}_6\text{H}_{14}\text{O}$, and 2,4-dimethyl-6-heptanol, $\text{C}_9\text{H}_{20}\text{O}$, are obtained. The latter has not been prepared before. The equations are:—



The properties of $\text{C}_6\text{H}_{14}\text{O}$ have already been studied. $\text{C}_9\text{H}_{20}\text{O}$ is a colourless liquid with a pleasant odour. When oxidised with chromic mixture it yields 2,4-dimethyl-6-heptanone. Its semicarbazone forms almost insoluble colourless crystals.

Iso-indogenides.—A. Wahl and P. Bagard.—The iso-indogenide of aromatic aldehydes can be prepared by the condensation of an oxindol with the aldehyde in an alcoholic medium. The derivatives of benzaldehyde and anisic aldehyde are coloured, which shows that the benzaldehyde-oxindol molecule is a chromogenic molecule. The hydroxyl-iso-indogenides are yellow compounds, the nature and position of the auxochrome groups having little influence on the tint of the product.

Berichte der Deutschen Chemischen Gesellschaft.

Vol. xlii., No. 11, 1909.

Constituents of Extract of Meat.—R. Engeland.—Among the basic constituents of Liebig's extract of meat a base of formula $\text{C}_7\text{H}_{15}\text{NO}_3$ occurs in large quantities. The name carnitine has been suggested for it. From its reactions it is found that—(1) it contains a carboxyl group; (2) it contains a hydroxyl group in the α -position with regard to the carboxyl; (3) it contains a trimethylamine residue bound to the carbon atom which is in the γ -position with regard to the carboxyl group. Thus it is an α -oxy- γ -trimethylaminobutyric acid of normal structure. Its chloride has the formula $\text{Cl}(\text{CH}_3)_3\text{N} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{COOH}$.

Preparation of Pyrrol.—Eugen Khotinsky.—When the ammonium salt of mucic acid is heated with a little glycerin a small yield of pyrrol is obtained, but if excess of glycerin is used the yield is greater. The reaction begins at 170° , and most of the glycerin distils over between 180° and 210° . The rôle of the glycerin is to keep the volatile ammonia in solution, whereas in dry distillation the greater part of it is lost and the yield of pyrrol is smaller. The amount of pyrrol obtained is considerably increased if the glycerin used for the experiment is previously saturated with ammonia gas.

Hydrazo- and Azomethane.—Johannes Thiele.—The decomposition product of dimethylnitroso-hydrazine is the dichlorhydrate of hydrazomethane, which, on oxidation with potassium chromate, gives azomethane, $\text{CH}_3 \cdot \text{N}_2 \cdot \text{CH}_3$, a colourless soluble gas of boiling-point 1.5° . The gas is explosive, and burns with a very luminous flame. When it is diluted with carbon dioxide and heated it decomposes chiefly into nitrogen and ethane, ethylene and methane being also formed. $\text{CH}_3 \cdot \text{N}_2 \cdot \text{CH}_3 \rightarrow \text{N}_2 + 2\text{CH}_3$, $2\text{CH}_3 \rightarrow \text{C}_2\text{H}_6$, $2\text{CH}_3 \rightarrow \text{CH}_4 + \text{CH}_2$, $2\text{CH}_2 \rightarrow \text{C}_2\text{H}_4$. When exploded by an electric spark it gives hydrogen, ethylene, and methane.

THE CHEMICAL NEWS.

VOL C., No. 2602.

THE RATIO BETWEEN THE URANIUM AND RADIUM IN RADIO-ACTIVE MINERALS.

By Mdlle. GLEDITSCH.

In a former note I gave the preliminary results of researches on the ratio between the uranium and radium in radio-active minerals. As the results were not the same as those obtained by other chemists and physicists I thought it advisable to investigate whether the difference was due to the method, which was not the same as that employed in earlier experiments.

The method, which has already been described, consists in making a solution of a certain quantity of the mineral, adding to it a barium salt, and precipitating the barium, radium, and lead by means of sulphuric acid. The precipitate is boiled with an excess of sodium carbonate and soda, and is thus transformed into carbonates. When these carbonates are dissolved in a dilute acid a solution is obtained in which the radium can be determined by the emanation disengaged. This method is liable to three errors:—

The solutions in which the precipitations were effected might retain some radium. Some of the radium might pass into the solution of sodium carbonate with which the active sulphates were boiled. Finally, the minerals sometimes leave insoluble residues which might contain radium.

My researches show that only a very small correction, which does not alter the results previously given, must be made for the quantity of radium left in these different products. The solutions of the minerals retain a negligible amount of radium; I have never found more than 0.3 per cent of the total quantity, and usually less than 0.2 per cent. The solutions of sodium carbonate contain a larger proportion; however, I have never found more than one per cent of the total quantity, and when the same method of procedure is always adopted this quantity does not vary much for the different minerals. Finally, the residues which are really insoluble are only very small in amount, and even supposing that the activity which they retain is due entirely to a salt of radium, the necessary corrections are very small.

Thus I am led to conclude that there is no constant ratio between the uranium and radium in active minerals. Hitherto each mineral has given a definite value for the ratio. Thus I have found:—

	Ratio. Radium : Uranium.
French autunite	2.85×10^{-7}
Joachimsthal pitchblende	3.58×10^{-7}
Ceylon thorianite	4.19×10^{-7}

The constant ratio of the two metals in active minerals has hitherto been the principal fact upon which the theory of the production of radium by uranium is based. According to my experiments this fact is not true, although the numbers obtained are of the same order of magnitude. It may be suggested that the connection actually exists, and that radium is really a product of the disintegration of uranium, but that the mechanism of the transformation is not so simple as is generally supposed, or that some influences intervene to change the ratio between the two elements in radio-active minerals. The first results which have been obtained seemed to show that the ratio is greater the greater the antiquity of the mineral, and this might be explained by the fact that the formation of radium by uranium is much slower than has hitherto been believed;

for instance, it might be supposed that intermediate products exist having a life which is long compared to that of uranium.

In the second place the question arises whether the rapidity of the transformation is an absolute magnitude independent of exterior circumstances, and if in particular it does not depend upon the presence of certain elements in the mineral, *e.g.*, of thorium or actinium.

No decided opinion can be expressed on this subject until the exact ratio is known for a great number of minerals.

An important consequence of these researches is that the determination of the mean life of radium based upon the existence of a constant ratio between the uranium and radium in the minerals cannot be considered exact.—*Comptes Rendus*, cxlix., 267.

NUTS YIELDING BORNEO TALLOW.

By CLAYTON BEADLE and HENRY P. STEVENS.

We had occasion to examine a quantity of Borneo tallow extracted from the *Shorea gysbertiana*, which was found in every way to closely resemble the results given by Lewkowitsch, showing it to be eminently adapted for candle making, soap making, and as an ordinary burning oil without smoke.

From various sources we have ascertained that the following plants yield nuts from which Borneo tallow can be extracted:—

Botanical Names.

<i>Shorea stenoptera</i>	<i>Shorea compressa</i>
„ <i>aptera</i>	„ <i>gysbertiana</i>
<i>Hopea aspera</i>	„ <i>Scarrbertiana</i>
<i>Isoptera Borneensis</i>	„ <i>Martiniana</i>
	„ <i>falcifera</i>

We are indebted to the Director of Kew Gardens for three of the nuts, which we examined with the following results:—

	<i>Isoptera</i> <i>Borneensis</i> .	<i>Shorea</i> <i>stenoptera</i> .	<i>Shorea</i> <i>aptera</i> .
	Per cent.	Per cent.	Per cent.
Moisture	10.0	10.0	10.0
Oil	58.0	64.6	49.9
Albumenoids	7.2	8.7	5.5
Ash	0.8	0.5	1.2
Indigestible matter	9.9	8.1	5.0
Carbohydrates (by diff.)	14.1	8.1	28.4
	100.0	100.0	100.0

The amount of oil yielded on pressing	48—52	55—60	41—45
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The residue after pressing consists approximately as follows:—

Moisture	10.0	10.0	10.0
Oil	10.0	10.0	10.0
Albumenoids	18.0	24.0	10.0
Ash	2.0	2.0	2.0
Indigestible matter	25.0	27.0	10.0
Carbohydrates (by diff.)	35.0	27.0	58.0
	100.0	100.0	100.0
Food units	105.0	112.0	108.0

From information we received from Sarawak the exportation of Borneo tallow for the first nine months of 1908 amounted to 2500 tons, most of which appears to go to Antwerp, and that ten times the amount now collected could be obtained by systematic treatment.

A SIMPLE METHOD FOR DETERMINING VAPOUR-DENSITIES AND FOR ANALYSING BINARY MIXTURES. (EIGHTH COMMUNICATION).

By PHILIP BLACKMAN.

THIS paper has been constructed in compliance with several requests to compile a complete account of the essential portions of the non-special method apparatus from a practical point of view (*i.e.*, for laboratory and experimental purposes), similar to the description of the special apparatus published in the *CHEMICAL NEWS*, 1909, c., 13, 129. All discussions and proofs of formulæ, together with illustrative data of experimental determinations, are here omitted, but full references to all these matters are here given. (For results see *Zeit. Phys. Chem.*, 1908, lxi., 52, 53, 637, 638; 1909, lxx., 551; *Journ. Phys. Chem.*, 1908, xii., 665, 669, 675, 677; 1909, xiii., 139, 140, 141).

Apparatus.

The apparatus consists of two parts—a manometer (or pressure-gauge) and a bulb.

Manometer, or Pressure-gauge.

The manometer consists of a glass capillary tube, somewhat shorter than the length of the body of the vessel, closed at one end and having a mercury-thread in the bore

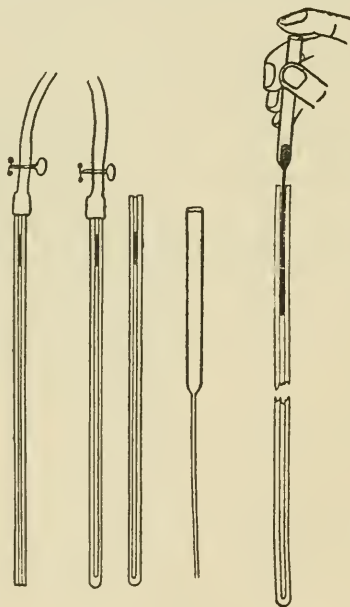


FIG. 1. FIG. 2. FIG. 3. FIG. 4.

near the other end. It may be made by one of the three following methods, of which the second is perhaps the easiest as regards manipulation:—

1. One end of a piece of capillary tubing of the proper length is sealed off in a flame. The tube is warmed in a flame, and the open end placed in some clean dry mercury; as the glass cools, the air within contracts and a thread of mercury is drawn in.
2. A piece of rubber tubing is fixed on to one end of the capillary tube, and a thread of mercury sucked up through the other end; the mercury is drawn in until it reaches a short distance from the rubber-fixed end, and the rubber tube is then closed by means of a clip or pinchcock (see Fig. 1). The

other exposed end is now sealed off in the blowpipe flame (see Fig. 2), the clip or pinchcock is removed, and the rubber tube taken off.

3. If the bore of the capillary tube is not too narrow, one end is sealed off in the blowpipe flame. A re-fill (see Fig. 3) is made by softening in the flame one end of a piece of glass tubing and drawing it off to a long fine capillary end. A little mercury is sucked up into it, and kept within by placing the forefinger over the wide end; the narrow end is then inserted in the bore of the capillary tube, and when it has reached the desired position there, the hold of the finger is slightly eased, which will allow a thread of mercury to run into that part of the bore (see Fig. 4).

Method.

1. The manometer must be allowed to cool to room temperature, placed in a horizontal position, and the length L , measured in mm., of the enclosed air-thread determined by means of a mm. scale or measure (see Fig. 5).
2. The substance to be experimented on is weighed out (weight = w) in a small stoppered glass weighing-bottle.

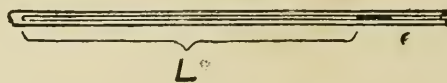


FIG. 5.

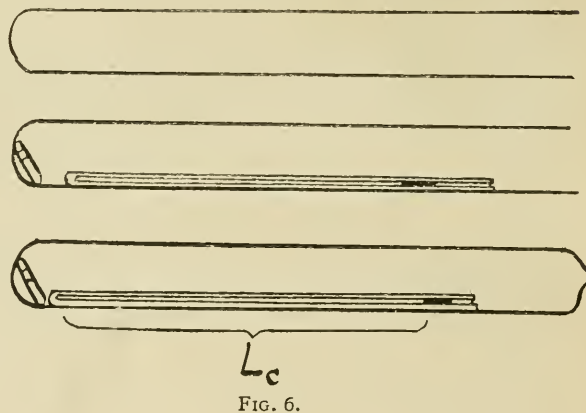


FIG. 6.

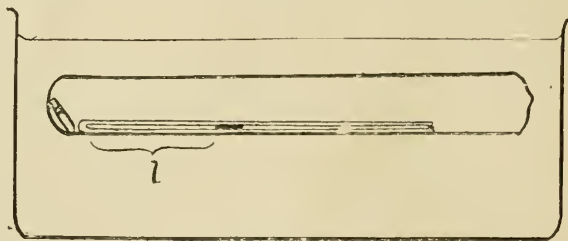


FIG. 7.

3. A glass tube, at least 10 cm. longer than the manometer and considerably wider than it, is thoroughly cleaned and dried, and one end sealed up (see Fig. 6). It is allowed to cool, and the manometer and the weighing-bottle with its contained known weight of the substance to be experimented on are introduced into the tube (see Fig. 6), and the open end carefully sealed up. When it has cooled to room temperature it is placed in a horizontal position, and the length L_c (measured in mm.) of the manometric air-thread is determined.

4. The external temperature, t_1 , and atmospheric pressure, p , in mm. are determined.

5. The vessel is heated in a horizontal position, in a suitable heating-jacket in the vapour of some substance boiling at a temperature above that at which the substance experimented on vaporises at ordinary atmospheric pressures, or better in a thermostatic trough containing some convenient heating medium such as glycerin or paraffin wax. When the substance has completely vaporised and the mercury index within the manometer has become stationary, the length, l , in mm. of the manometric air-thread is measured by means of callipers, compasses, or dividers, the distance between whose feet is then measured off along a mm. scale (see Fig. 7).

6. The bulb or vessel is removed, allowed to cool, and opened by cutting away a small portion of the glass at the end. The tube is placed in an upright position, with the hole to the top (the manometer and weighing-bottle must not be removed), and water poured in to fill it completely from a burette. The volume of water poured in represents the volume, V , occupied by the heated gases. (If on opening too great a piece of the tube has been cut off, the volumes of the greater and smaller portions are determined separately, and their sum is equal to V . The opening is best effected by making a clean file-mark round the part to be opened, and touching it with the red-hot end of a piece of glass rod).

Precautions.

1. Only absolutely dry clean mercury must be used.
2. The capillary tube employed for the manometer must be perfectly clean and dry.
3. The temperature t_2° , to which the bulb is heated, is not required to be known, unless for special purposes. See the end of the paper. (See *Zeit. Phys. Chem.*, 1908, lxiii., 50; *Journ. Phys. Chem.*, 1908, xii., 668, 670, 671, 673).
4. The apparatus may be used to experiment upon substances which under ordinary conditions react chemically upon mercury. (Consult *Zeit. Phys. Chem.*, 1908, lxiii., 637; 1909, lxx., 551; *Journ. Phys. Chem.*, 1908, xii., 673).
5. The thread of mercury in the manometer should originally be not less than 3 or 4 cm. from the open end of the manometer. (Refer to *Zeit. Phys. Chem.*, 1909, lxx., 549; *Journ. Phys. Chem.*, 1908, xii., 673).
6. Capillary tubing of too great a wall-thickness should not be used for making the manometer.
7. There is no need whatever for employing thick-walled or Jena tubing from which to make the bulb; any kind of tubing (of not too thin walls) will do perfectly well, especially that which will give no trouble in sealing up or re-opening.

Vapour Densities.

(For proofs see *CHEMICAL NEWS*, 1909, xcix., 87; *Zeit. Phys. Chem.*, 1908, lxiii., 49, 51; *Journ. Phys. Chem.*, 1908, xii., 662).

If the vapour-density be d its value is to be calculated from the formula—

$$d = \frac{31068 w l L_c (273 + t_1)}{p L V (L_c - l)}$$

Binary Mixtures.

(For proofs see *Zeit. Phys. Chem.*, 1908, lxiii., 52, 638; *Journ. Phys. Chem.*, 1908, xii., 670, 676; 1909, xiii., 426).

The experiment is carried out as already shown. If the required percentage weights of the two constituents be w_1 and 100 w_1 , the respective vapour-densities (supposed known) being d_1 , d_2 , the calculations are effected by means of the formula—

$$d_2 w_1 + d_1 (100 - w_1) = \frac{100 d_1 d_2 p L V (L_c - l)}{31068 w l L_c (273 + t_1)}$$

This formula may also be employed in determining the extent to which a substance, easily decomposed into two components when brought into the gaseous condition on heating, dissociates into its binary constituents.

The apparatus may also be employed to determine the

amount, q , of a volatile component, of vapour-density, d , assumed known, given off on heating a compound to varying temperatures (e.g., to measure the quantity of water-vapour evolved from $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), the necessary calculation being carried out by aid of the formula—

$$q = \frac{d p L V (L_c - l)}{31068 l L_c (273 + t_1)}$$

Internal Pressures.

The internal pressure (in atmospheres) π , corresponding to the given readings as found, is given by the formula $\pi = pL(273 + t_2)/760l(273 + t_1)$, t_2 being the temperature to which the vessel is heated.

The author must point out that there is no similarity whatever, either as regards apparatus, theory, or manipulation, between this method, viz., "A Simple Method for Determining Vapour-densities and for Analysing Binary Mixtures" (which, incidentally, is entirely original and has not the slightest connection with any other vapour-density method), and the author's "A New Method for Determining Vapour-densities" (see *Ber.*, 1908, xli., 768, 881, 1588, 2487, 4141; *Journ. Phys. Chem.*, 1908, xii., 679; 1909, xiii., 433). These two totally distinct methods are confused, and made to appear as if they were one and the same method, both in R. Meyer's *Fahrbuch der Chem.* (1909, p. 11), and the Chemical Society's *Report on the Progress of Chemistry for 1908* (1909, v., 200).

Hackney Technical Institute, London, N.E.

ON JAFFÉ'S COLORIMETRIC METHOD FOR THE ESTIMATION OF CREATININE.

By A. CHASTON CHAPMAN.

THE author has shown that the red coloration on which this method is based depends, not on the formation of creatinine picrate, but is due to the reduction of the picric acid in alkaline solution to a mixture of amido-dinitrophenol (picramic acid) and diamido-nitrophenol, the alkali salts of which are deeply coloured. The same coloration is produced by numerous reducing agents, such as nascent hydrogen, hydroxylamine, acetone, aldehyde, ammonium sulphide, and titanium trichloride. Creatinine acts as a powerful reducing agent, and if it is present in excess the picric acid may undergo reduction to colourless triamido-phenol. Colour measurements showed the red coloration to be due to both the monamido and the diamido phenol, and that solutions of the sodium salt of picramic acid could not be used for matching purposes. Since the coloration is due to a somewhat complex reducing action, it is clear that the conditions under which the test is carried out must be fairly closely defined if accurate results are to be obtained.

Influence of Temperature.—This factor is of considerable importance, since up to a certain point the colour is increased, after which there is a reduction due to the formation of triamido phenol.

Influence of Time.—This factor is of much less importance than the preceding, and slight differences have no appreciable influence on the results. The general effect is, however, of the same character as in the case of the temperature factor—that is to say, there is at first an increase and then a reduction of the colour intensity.

Influence of the presence of Dextrose.—As in certain commercial products, dextrose and creatinine may occur together, experiments were made to ascertain whether the former substance exerted any influence on the estimation of the latter. It was found that in the cold, and under the ordinary conditions of the test, dextrose was without appreciable effect.

In conclusion, attention is called to the necessity of working in sufficiently dilute solutions, in analysing highly coloured products, since the disturbing effect of the colour may be very considerable.

NOTE ON THE DETECTION OF SODIUM
SULPHITE IN THE PRESENCE OF SODIUM
SULPHATE AND SODIUM THIOSULPHATE.

By FRANK E. WESTON, B.S., F.C.S.

SEVERAL methods have been described in recent times for detecting and estimating the constituents of mixtures containing two or more of the following:—Sulphides sulphites, thiosulphates, and sulphates of the alkali metals.

Some of the methods give accurate results when close attention is paid to the exact conditions laid down for performing the reaction, but most of them are methods requiring much time, and several fail to detect small quantities of sulphite in presence of a thiosulphate and a sulphate.

Autenreith and Windaus (*Journ. Chem. Soc. Abst.*, 1898, ii., 452) detect sulphite in the presence of thiosulphate by adding to the solution of the two excess of a solution of $\text{Sr}(\text{NO}_3)_2$, well shaking, and filtering; a precipitate of SrSO_3 is thus obtained, whilst Sr_2SO_3 remains in solution; the solubility of the two salts are given as 1 part of SrSO_3 in 30,000 of water, and 1 part of Sr_2SO_3 in 3.7 parts water.

Browning and Howe (*Journ. Chem. Soc. Abst.*, 1898, ii., 124) precipitate the sulphite in acetic acid solution with BaCl_2 , filter, and treat filtrate with a slight excess of iodine to convert sulphite into sulphate, take up excess of iodine with SnCl_2 solution, and then acidify with a few drops of HCl ; a white precipitate indicates a sulphite; filter, and treat filtrate for thiosulphate.

Bloxam (*CHEMICAL NEWS*, lxxii., 63) gives details of a scheme for detecting sulphites, hydric sulphide, hydrosulphides, polysulphides, thiosulphates, and sulphates in the presence of each other, the sulphite being detected by means of nitroprusside, a method given by Fresenius in his "Qualitative Chemical Analysis."

The great difficulty in all these methods is to detect the sulphite in the presence of the sulphate and thiosulphate.

The author with Mr. C. W. Jeffreys (*CHEMICAL NEWS*, xcvi., 85) have described a method of detecting sulphite in the presence of the other two, even when the sulphite occurs in small quantities, depending upon the insolubility of PbSO_3 in a solution of $\text{Na}_2\text{S}_2\text{O}_3$, and the solubility of PbSO_4 and PbS_2O_3 in the same.

Another simple test has been arrived at which easily detects a sulphite of the alkalis in the presence of sulphates and thiosulphates of the alkalis. Mr. C. W. Jeffreys has thoroughly tested the reaction, and all three acids can be easily detected in mixtures of the alkali salts of the same with great ease.

It is well known that solutions of Na_2SO_3 are oxidised to Na_2SO_4 by solutions of I , and methods have been devised for applying this principle to the estimation of solutions of the alkaline sulphites. Ashley (*Am. Journ. Sci.*, 1905, [5], xix., 237; and xx., 13) adds twice the quantity of I solution necessary to oxidise the Na_2SO_3 to a solution of the sulphite containing NaHCO_3 , carefully acidifies with dilute HCl (1:4), and titrates excess of iodine with $\text{Na}_2\text{S}_2\text{O}_3$. When a solution of I in KI solution is added to a solution of Na_2SO_3 the following reaction occurs:— $\text{Na}_2\text{SO}_3 + \text{H}_2\text{O} + \text{I}_2 = \text{Na}_2\text{SO}_4 + 2\text{HI}$. Hence the solution which was originally neutral or alkaline becomes acid; a method of estimating a solution of Na_2SO_3 is based on this principle (*Journ. Chem. Soc. Abst.*, 1898, ii., 91), and consists of first adding $\text{N}/10$ H_2SO_4 to the solution to convert the Na_2SO_3 into NaHSO_3 , then adding standard I till following reaction is complete:— $\text{NaHSO}_3 + \text{H}_2\text{O} + \text{I}_2 = \text{NaHSO}_4 + 2\text{HI}$, and finally determining the acidity of the solution (HI) by $\text{N}/10$ NaOH .

Now, if insufficient I solution be added to a sulphite solution to convert the latter into sulphate, the HI produced reacts upon the remaining Na_2SO_3 with the formation of a solution of SO_2 or $\text{Na}_2\text{SO}_3 + 2\text{HI} = 2\text{NaI} + \text{H}_2\text{SO}_3$. The SO_2 thus formed may be detected as follows:—

- i. Well shake and smell; if the solution is not too weak the odour of SO_2 is observed.
- ii. If the resulting solution is too weak to give the odour of SO_2 , add drop by drop a weak solution of $\text{K}_2\text{Cr}_2\text{O}_7$, when the pale green coloration due to formation of salts of basic Cr is immediately produced.

Now, the reaction of I solution with $\text{Na}_2\text{S}_2\text{O}_3$ solution gives a neutral solution; hence no SO_2 is produced, and therefore no reduction of $\text{K}_2\text{Cr}_2\text{O}_7$ solution on addition of same (after some time a turbid brown coloration is produced). The reaction of I solution on Na_2SO_4 solution is nil.

Hence the method of applying the test is as follows:—Prepare a solution of the substance in water of about 5 per cent strength. To 5 cc. of this solution add a solution of I in KI ($\text{N}/10$ I is most convenient); if decolorised continue till faint trace of I is obtained (presence of sulphite or thiosulphate or both); test this solution as to acidity, and if found to be acid the probable existence of a sulphite is indicated. To another 5 cc. of the original solution add half the quantity of I solution as used in the first test, well shake, and test for SO_2 by smell and by adding dilute $\text{K}_2\text{Cr}_2\text{O}_7$ solution drop by drop as described above. If pale green coloration produced, SO_2 is present, and hence a sulphite. If no coloration, then a thiosulphate is present. The sulphate can be detected by the BaCl_2 test, and the thiosulphate confirmed by the usual tests even in the presence of sulphite.

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A LITTLE PROBLEM AND ITS APPLICATION
TO CHEMISTRY.

By FRANK HEALY.

A RING of elastic material, as steel, for instance, vibrates when struck, having a number of quiet nodes distributed at regular intervals and separating the vibrating segments. If now we conceive of an electric current flowing in the ring as in a single loop of the wire of an electromagnet, we can readily picture the field of force due to the current. This completes the conditions upon which the following problem is based. What combinations of these rings will possess stability, disregarding all conditions except mechanical vibration of the elastic material and the presence of the magnetic field of force? The rings are assumed to be all alike in every respect. The problem is not complicated or difficult, but so simple that even a child, if given the rings and understanding the conditions, could by repeated trials soon arrive at the correct solution. One quickly finds that all possible combinations of 2, 3, 4, 5, 6, and 7 rings are unstable by reason of either magnetic repulsion or mechanical vibration. A combination of eight rings is remarkably stable, and is, in fact, the structure of maxim stability. The rings are arranged like the eight circles inscribed on the faces of a regular octahedron. The structure is octopolar, having eight fields of force, and the centres of the rings, the centres also of the fields of force, are arranged like the eight corners of a cube. Four are of one polarity, while the other four are of opposite polarity, and each four are arranged like the apices of a regular tetrahedron. The algebraic sum of the values of the internal fields of the structure is zero, the algebraic sum or effective value of the external fields is also zero.

In general, an octopolar system having such an arrangement of its fields of force has this property, that if the value of all the fields be doubled in succession, then tripled, quadrupled, &c., the effective values of the total field of force of the system pass repeatedly through the following series, m being the unit field of force:— $m, 2m, 3m, 4m$; $3m$ and one self-balanced or latent pair, $2m$ and two latent pairs, m and three latent pairs, and 0 or four latent pairs. This series is repeated as often as the unit field of force can be added in succession to the eight poles of the

structure. Now, this series is identical with the normal succession of valence in the Periodic Table. Moreover, all that is known of the space relations of the valence bonds of the carbon atom and other atoms is in agreement with the space relations of the forces of the corresponding members of this octopolar structure. That additional rings can be added to the eight-ring structure to form very stable combinations, and give the series as above, becomes apparent when one constructs a model of the structure. It will suffice to state here that the external arrangement remains the same substantially, while the original rings become in succession moved nearer the centre of the structure.

The ring itself appears to correspond to the particle of the α -ray, since it must inevitably become transformed into the eight-ring structure corresponding to the helium atom. The particle of the β -ray, or cathode ray, called the corpuscle, or more generally the electron, being considered identical to the theoretical electrical unit, may give rise to the ring by its properties while in motion. For instance, although two electrons mutually repel one another because of their electronegative charges, the repulsion is more or less balanced by magnetic attraction if moving side by side in parallel paths, while at the velocity of light they cease to repel. If the electron should rotate a magnetic field of force would be produced so that the magnetic axis coincides with the axis of rotation. In an electropositive field of force the little magnets would combine to form long chains. If this chain is moving rapidly in the direction of its length, and then forms a closed loop or ring by union of its ends, in the presence of sufficient positive electricity to balance the charges of the electrons, the resulting ring would have the properties required to account for the more fundamental characteristics of the members of the Periodic Table. To have the necessary ratio between thickness and diameter there must be about 280 corpuscles in the ring. Knowing the relative mass of the corpuscle it can be seen how the rings contribute to the total mass of the atoms. Although the ring structure would furnish the fundamental characteristics of the atom, it would not necessarily constitute the greater portion of the mass. Doubtless many circuits of corpuscles with their complement of positive electrification would find stable positions within and about the ring structure, modifying the normal characteristics and giving to the atoms of each kind their own peculiarities.

This conception of valence is in agreement with the view usually held which regards unit electrostatic charges on the atom as governing valence, rather than being the result of more fundamental conditions. A rigorous sorting of the valence bonds of the elements into "electropositive" and "electronegative" has not been possible with any great success. Especially in organic compounds, it often happens that electropositive and electronegative atoms and radicals can replace one another indiscriminately. Elements like nitrogen, phosphorus, oxygen, and sulphur, which would be classed as electronegative, actually confer very strong electropositive properties on some of their compounds, as the ammonium, phosphonium, oxonium, and sulphonium derivatives. This suggests that it is the presence of latent pairs of valence bonds (like unsaturated valence bonds in organic compounds) that confers the electronegative tendencies on an atom or group of atoms. There is no conclusive evidence that atoms or radicals possess charges before becoming ionised by scission of the neutral molecule in which they occur.

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Double Sulphates.—M. Barre.—Strontium sulphate very readily gives a double sulphate with potassium sulphate, the formula of which is $K_2SO_4 \cdot SrSO_4$ without water of crystallisation. A similar double sulphate of ammonium and strontium exists of formula $SrSO_4 \cdot (NH_4)_2SO_4$. Potassium and ammonium sulphates also form similar compounds with lead sulphate, but no compound of lead sulphate and sodium sulphate appears to exist.—C. R., cxlix., No. 4.

THE ESTIMATION OF IRON BY PERMANGANATE IN PRESENCE OF HYDROCHLORIC ACID.*

By G. CECIL IONES, A.C.G.I., F.I.C., and JOHN H. JEFFERY.

(Concluded from p. 165).

Experimental.

WE have reduced our experimental record to just so much as is necessary to support our conclusions and to enable anyone to repeat our more instructive experiments. The following tables are compiled from experiments made within the last few days with the special object of saving our readers' time. The results published here find confirmation in many other series of experiments, made with solutions not exactly equivalent, and therefore requiring closer inspection to learn their bearing than the busy reader can well spare. Needless to say, many of our early series of experiments, made when our knowledge was less complete, are less regular; but our purpose is to show how permanganate can be used in presence of hydrochloric acid, and not how we obtained this knowledge.

The following solutions were used:—

Manganese Solution.—Reinhardt's solution, the preparation of which has already been described.

Stannous Chloride.—50 grms. of the crystallised salt and 100 cc. of concentrated hydrochloric acid made up to 1000 cc.

Mercuric Chloride.—A cold saturated solution.

Hydrochloric Acid.—6-normal, that is to say, acid of specific gravity 1.1, or about the strength of the mixture, which exhibits a constant boiling-point.

Sulphuric Acid.—Also, for convenience of comparison, about 6-normal.

In each of the experiments recorded in Table I., the quantity of water stated in column B was mixed in a capacious basin with the Reinhardt solution, where this was used, and tinted with permanganate, of which one drop sufficed in every case; 25 cc. of a freshly prepared solution of ferrous ammonium sulphate was then added, and simultaneously the acid, hydrochloric or sulphuric, as the case might be. Where stannous chloride or mercuric chloride were used, these were added with the acid as follows:—Ten minutes before each titration was made, the requisite amount of hydrochloric acid was placed in a flask, and the stannous chloride and mercuric chloride added. This mixture was added to the contents of the titration bowl simultaneously with the ferrous solution. The permanganate was then allowed to fall drop by drop into the bowl with constant stirring, each titration occupying about four minutes. All the numbers in the table in columns A to H represent cubic centimetres.

Experiments 2 and 3 compared with 1 appear to confirm the observation of Harrison and Perkin that Reinhardt's solution exerts an oxidising action on the iron solution; but the solution used in this particular series of experiments had no such action as experiment 4 shows, where doubling the volume of Reinhardt's solution does not affect the result. Had the sulphuric acid contained ferrous iron, as it frequently does, experiments 5 and 6 would have shown higher results than experiment 1. That they give identical numbers, higher than that found in experiment 1, only illustrates the fact to which Treadwell has already drawn attention, that to obtain accurate results by Marguerite's method, it is necessary to have much sulphuric acid present, the minimum allowable strength being about half-normal. Larger quantities of sulphuric acid are without influence on the result. Experiment 7 may appear a surprisingly good result to some who have studied the influence of hydrochloric acid on permanganate titrations of iron. Harrison and Perkin record an excess consumption of permanganate of 0.6 cc., with only one-fourth as much hydrochloric acid present. The difference between their results and ours is, we believe, due to

* From the Analyst, July, 1903.

TABLE I.

No. of experiment.	A. Reinhardt's solution.	B. Water.	C. 6N H ₂ SO ₄ .	D. 6N HCl.	E. SnCl ₂ solution.	F. HgCl ₂ solution.	G. Final volume.	H. Permanganate consumption.
1.	—	425	25	—	—	—	500	25'05
2.	25	400	25	—	—	—	500	25'0
3.	25	425	—	—	—	—	500	25'0
4.	50	400	—	—	—	—	500	25'0
5.	—	400	50	—	—	—	500	25'0
6.	—	150	300	—	—	—	500	25'0
7.	—	425	—	25	—	—	500	25'5
8.	—	415	—	25	0'5	10	500	25'7
9.	25	400	—	25	—	—	500	25'05
10.	25	390	—	25	0'5	10	500	25'1
11.	50	365	—	25	0'5	10	500	25'1
12.	10	405	—	25	0'5	10	500	25'2
13.	25	340	—	25	0'5	60	500	25'1
14.	25	390	—	25	—	10	500	25'05
15.	25	365	—	50	0'5	10	500	25'15
16.	50	340	—	50	0'5	10	500	25'1
17.	25	405	—	10	0'5	10	500	25'05
18.	25	390	—	25	1'0	10	500	25'15
19.	25	390	—	25	2'0	10	500	25'25
20.	25	900	—	25	0'5	10	1000	25'1
21.	25	1400	—	25	0'5	10	1500	25'15
22.	25	90	—	25	0'5	10	200	25'05

difference in manner of adding the permanganate. By running this in a continuous stream up to 23 cc., and then proceeding by drops, we have obtained results practically identical with theirs. Experiment 8 shows that either stannic or mercuric or mercurous chloride, all of which are present in practical titrations, reinforce the disturbing action of the hydrochloric acid. Experiment 9 shows that 25 cc. of Reinhardt's solution reduces the error introduced by 25 cc. of hydrochloric acid to 0'05 cc., whilst experiment 10 shows that it does not wholly neutralise the action of the tin or mercury salts. Experiments 11 and 12 show that, while no advantage is gained by increasing the proportion of Reinhardt's solution, it is not wise to diminish it greatly below that used in experiment 10. Experiment 13 shows that no advantage attends the use of large quantities of mercuric chloride, such as the 60 cc. used by Reinhardt and by most workers since his time. Experiments 15 and 16 show that doubling the amount of hydrochloric acid, whilst preserving unaltered all the other conditions, increases the over-consumption of permanganate from 0'1 to 0'15, but that this can be prevented from exceeding 0'1 by taking more of Reinhardt's solution. Experiment 17 shows how the over-consumption of permanganate falls when the amount of hydrochloric acid is greatly reduced. Experiment 14, compared with No. 9, shows that mercuric chloride, as might be expected, has no influence on the titration, whilst Nos. 18 and 19 show that either stannic or mercurous chloride has a notable influence. Experiment 20 shows that dilution considerably beyond 500 cc. is without influence, whilst Nos. 21 and 22, like the figures of Zimmermann, Harrison and Perkin, and Birch, directly challenge the recommendation to be found in all the text-books from the time of Fresenius, that the titration is best conducted in highly dilute solution. The greater the dilution the wider the divergence from Marguerite's equation. In practice, however, a final volume of about 500 cc. is preferable, since comparatively wide variations from this volume have no measurable influence on the result. In a bulk of 1500 cc., such as Reinhardt recommended, one drop of permanganate is scarcely enough to produce a distinct pink tint, whilst in small bulks, under 200 cc., though with great care the absolute error may be very slightly reduced, it is more difficult to get closely concordant duplicates, especially if the amount of hydrochloric acid is large.

A number of the experiments of Table I. were next repeated with the following modification:—The measured 25 cc. of ferrous solution was completely oxidised, mixed

with the quantity of hydrochloric acid stated in column D, heated to boiling, and reduced by stannous chloride, which towards the end was added two drops at a time. When two drops of stannous chloride produced no further change of tint, a measured excess of the reagent was added, the solution cooled, and subsequently mixed with mercuric chloride. After ten minutes, the contents of the flask were emptied into a bowl containing the Reinhardt solution and water previously tinted by one drop of permanganate. The results of experiments 10 to 13 and 15 to 19 were confirmed in every case. Since the experiments of this series differed from those in Table I. by the presence of some 25 cc. of N/10 stannic chloride, it may be taken that this reagent has, as might be expected, no influence on the course of the titration. On the contrary, it seems to be conclusively proved that mercurous chloride has a marked influence if present in large amount. The excess of stannous chloride can easily be kept below 0'25 cc., and the results differ inappreciably when the excess is varied from 0'1 to 0'5 cc. The interval of ten minutes between the addition of the mercuric chloride and the commencement of the titration is the result of our observation that, when the excess of stannous chloride is purposely kept very small, the precipitate of mercuric chloride takes an appreciable time to appear. From this we were led to suppose that the reaction $\text{SnCl}_2 + 2\text{HgCl}_2 = \text{SnCl}_4 + 2\text{HgCl}$ might require an appreciable time to approximate completion, and this we find to be the case. Titration of the liquid immediately after the addition of the mercuric chloride leads to high results, due to the presence of unoxidised stannous chloride. We find that Reinhardt knew that the reaction $\text{SnCl}_2 + 2\text{HgCl}_2 = \text{SnCl}_4 + 2\text{HgCl}$ never even approximated completion in dilute solutions, and he insisted on the addition of the mercuric chloride before diluting largely, but even in a bulk of 100 cc. the reaction is slow. Probably ten minutes is an unnecessary allowance, but it has been found to be both ample and safe, since no appreciable oxidation of iron takes place in a much longer time, identical results being obtained after thirty minutes standing.

In a further series of experiments, recorded in Table II., varying quantities of ferrous solution were titrated with permanganate under the conditions indicated in experiment 10 of Table I. Here, again, two methods were followed—namely, (1) Simple mixture of the ferrous solution with hydrochloric acid, mercurous and mercuric chloride, followed by titration in presence of Reinhardt's solution; and (2) titration of the ferrous solution by per-

manganate in presence of a little sulphuric acid, reduction of the resulting ferric solution by stannous chloride in presence of 25 cc. of hydrochloric acid (specific gravity 1.1), treatment with mercuric chloride, and re-titration by Reinhardt's method. Had we contented ourselves with one of these methods only, our conclusions might perhaps have dissatisfied some; but, fortunately, the two methods give identical results. Table II. shows the permanganate consumption (a) in half-normal sulphuric acid solution, and (b) by Reinhardt's method.

TABLE II.
Consumption of N/10 permanganate.

N/10 ferrous solution.	(a) In H_2SO_4 solution.	(b) By Reinhardt's method.
50	50	50.1
20	20	20.1
10	10	10.1
5	5	5.1
2	2	2.1
1	1	1.1

We think these results show plainly that the small unavoidable error introduced by hydrochloric acid, even in presence of Reinhardt's solution, is a constant one, independent of the amount of iron present, and therefore easily corrected for. The correction, though small, cannot be omitted, as on a small amount of iron it represents a notable percentage.

We have made many preparations of Reinhardt's solution and, though we have occasionally found them to possess oxidising power when first made, this has never been so great as that observed by Harrison and Perkin. Moreover, before the solutions are a week old this oxidising power becomes so small as to be unmeasurable. It is true that we used the purest chemicals procurable, but since we have found it possible to cut down the quantities to be used in each experiment to less than half those proposed by Reinhardt, the extra expense involved by this is not great.

It is impossible to lay too much stress on the importance of adding the permanganate slowly, drop by drop. We were led to this discovery by differences between ourselves, which by a process of elimination were ultimately traced to the difference in the speed at which we ran in the permanganate. We have since found that this point has been dealt with very fully by Skrabal (*Zeit. Anal. Chem.*, 1903, xlii., 359). We think the results of Birch and of Harrison and Perkin are evidence that they, too, were ignorant of the work of Skrabal, and this is perhaps not surprising, since the literature of the subject these authors were studying is immense, and in the course of his fifty-page paper Skrabal records but one experiment with Reinhardt's solution, and makes no reference at all to the method of Fresenius. Some of the earliest authors—Löwenthal and Lensen, for instance—speak of the addition of permanganate "drop by drop slowly" as the custom in their time, but there is no evidence whatever that they realised that such procedure was of vital importance. On the contrary, their own poor results suggest that they themselves disregarded the custom.

For the estimation of iron in ferric oxide, or other substances most easily got into solution in hydrochloric acid, we recommend solution in 25 cc. of hydrochloric acid (specific gravity 1.1), reduction by stannous chloride, using as small an excess of this as is reasonably possible, and addition of 10 cc. of mercuric chloride solution when cold. Into a capacious bowl we bring 25 cc. of Reinhardt's solution and some 400 to 500 cc. of tap-water, and tint the mixture by the addition of permanganate, of which one drop should suffice. Ten minutes after the addition of the mercuric chloride to the ferrous solution, we pour the latter into the bowl, rinse the flask or beaker, and add the rinsings to the contents of the bowl, which are then titrated with permanganate, drop by drop, with constant stirring. From the burette reading we deduct 0.1 cc., and calculate

the amount of iron present by reference to the known titre of the permanganate as determined by titration against a ferrous solution free from hydrochloric acid. With the above-mentioned quantities we believe the method capable of giving results equal in accuracy to those obtained by any volumetric method, and it is not difficult to keep all the quantities sufficiently near those named. A final dilution of from 400 to 1000 cc. is without measurable influence on the result, and tap-water that supplied to our laboratory, at any rate—may replace distilled water without disadvantage. This has saved us the trouble of boiling and cooling out of contact with air the large volumes of water required by our experiments. The amount of acid need never be much less than 25 cc., for after solution of the iron oxide it can always be made up to its original volume with acid of constant boiling-point. If, on the other hand, it is necessary to use fuming acid, this will be down to the strength of constant boiling-point acid by the time solution is complete; and if its volume much exceeds 25 cc., all that is necessary is to add an equal volume of Reinhardt's solution instead of the usual 25 cc. The tin solution recommended by Treadwell is too strong, having regard to the great influence of relatively small amounts of mercurous chloride. Of our tin solution it is immaterial whether the excess used is one drop or ten—a sufficiently wide margin for anyone. Provided the amount of hydrochloric acid is not less than about 20 cc. (specific gravity 1.1), and that the volume of Reinhardt's solution is at least equal to that of hydrochloric acid, the consumption of permanganate will in every experiment be almost exactly 0.1 cc. in excess of that demanded by Marguerite's equation. In our hands it averages a little less than this, but is much nearer 0.1 than 0.05, and we do not feel justified in splitting drops.

There is much to be said for Brandt's proposal to adopt pure ferric oxide as a standard for determining the titre of permanganate solutions; but if this is done, it is preferable to record the true and not the apparent titre on the label, if the solution is to be used for general purposes and not merely for the analysis of ores. For example, if 0.3194 gm. pure ferric oxide, by Reinhardt's method, requires exactly 40.0 cc. of our permanganate, we do not label the solution "exactly decinormal," as Brandt would do, but calculate the true titre as 1 cc. = $\frac{0.3194}{39.9}$ gm. ferric oxide, or $\frac{0.2231}{39.9}$ gm.

iron. Provided that 0.1 cc. be always deducted from the observed permanganate consumption, the solution can then be used for the estimation of widely varying quantities of iron by Reinhardt's method.

If the use of freshly made manganese solution is unavoidable, the oxidising power of this can be determined in ten minutes by two experiments, like 3 and 5 in Table I., and allowed for if a measurable quantity.

Unlike Birch, we found no difficulty in repeating the experiments of Fresenius, and even obtained better results than Fresenius himself, due no doubt to the slow speed at which we added the permanganate. When, however, we came to apply Fresenius's recommendations practically, we were scarcely surprised to find the method break down. For in his experiments, after the first titration Fresenius contented himself with adding more ferrous solution, and made no further addition of acid. Now, the analyst, with his ferrous solution in one flask and hydrochloric acid in the other, would presumably never mix them, and in any practical application of Fresenius's method each addition of ferrous solution would be accompanied by the addition of more acid, and, as a rule, of mercurous chloride, stannous chloride being infinitely more convenient to use than zinc.

The following experiments represent an attempt to apply Fresenius's method under test conditions:—125 cc. of N/10 ferric chloride, containing hydrochloric acid equivalent to 75 cc. of constant boiling-point acid, was reduced by stannous chloride, and made up to 250 cc. with mercuric chloride solution. Successive portions of 50 cc. were then added to 1000 cc. of water and titrated slowly with permanganate.

1st 50 cc. required	25.7	cc. permanganate
2nd "	25.7	"
3rd "	25.75	"
4th "	25.8	"

Twenty-five cc. of the same decinormal ferric chloride, reduced and titrated by Reinhardt's method, required 25.1 cc. permanganate. In order to give the method of Fresenius every chance, the ratio of acid to iron in these experiments was kept as low as we find it can be kept in practice.

As has been said in the introduction, Fresenius gave no practical example of this method, but of his second method he gave two examples which he believed to be practical. But here, again, he dissolved iron in sulphuric acid, and added the resulting ferrous solution, without any simultaneous addition of hydrochloric acid, to the contents of the vessel in which the preliminary experiment had been made.

Conclusions.

The method of Fresenius gives erroneous results, and appears to have been founded on a misconception, and never until now put to a practical test.

The method of Reinhardt, though empirical and dependent for its successful application on somewhat rigid uniformity of procedure, is yet capable of yielding results little, if at all, inferior in accuracy to those given by the best volumetric methods.

Our work was undertaken with a practical object, and, though theoretical considerations helped us in the choice of experimental methods, we do not propose to add to the mass of theory which has been woven around this subject. We may, however, point out that our results are consistent with the theory of Manchot and Wilhelms (*Annalen*, 1902, cccxxv., 93), and that those recorded in Table II. appear to lend additional support to their view.

We take this opportunity of expressing our thanks to Mr. R. F. Easton for much useful help in the conduct of the large number of experiments which were found necessary to the completion of this work.

DISCUSSION.

Mr. W. C. BIRCH said he had had occasion to work on this subject, and the results might perhaps be interesting, as bearing on the action of the manganous sulphate, which was an essential constituent of the Zimmermann-Reinhardt reagent. In titrating with that reagent there was a distinct, though slight, evolution of chlorine, and a brown colour was produced in the solution even by a quite small excess of permanganate over the quantity required to oxidise all the iron present. These brown solutions were very similar in appearance to those described by Pickering (*Journ. Chem. Soc.*, 1879, xlii., 654), which were produced by the action of hydrochloric acid on any of the higher oxides of manganese. Unfortunately, it was not possible to isolate this brown colouring matter from such dilute solutions as were met with in volumetric analysis; but, by blowing hydrochloric acid into a concentrated solution of potassium permanganate, and cooling the solution with ice and salt, it was possible to isolate a crystalline double salt having the formula $\text{MnCl}_2 \cdot 2\text{KCl} \cdot \text{H}_2\text{O}$. The reaction which caused the formation of this compound could perhaps be represented by the equation $\text{K}_2\text{Mn}_2\text{O}_8 + 16\text{HCl} = 2\text{KCl} + 2\text{MnCl}_3 + 8\text{H}_2\text{O} + 4\text{Cl}_2$. It had been shown by Rice (*Journ. Chem. Soc.*, 1898, lxxiv., 260) that manganous chloride reacted, though but slowly, with free chlorine at the ordinary temperature to produce MnCl_3 . He thought it fair to assume that under the conditions of the Zimmermann-Reinhardt titration the chlorine liberated would be in a nascent state, and would therefore be more active chemically than chlorine in the free state; and if that were so, it was to be expected that the reaction between the manganous sulphate or manganous chloride and the chlorine would go on more quickly than under the conditions of Rice's experiments. The Zimmermann-Reinhardt reagent, therefore, provided every chance for the

chlorine to enter into combination before escaping from the solution, and to remain in the solution in a state in which it was able to oxidise the remainder of the ferrous iron. This was shown by the following simple experiment which he had made:—About 10 cc. of concentrated hydrochloric acid, with a few cc. of potassium permanganate, were placed in one flask, and in another flask the same quantities of these reagents, with an excess of manganous sulphate, a current of air being aspirated through both flasks, and the evolved chlorine collected in potassium iodide, and titrated with thiosulphate. The chlorine evolved from the flask not containing manganous sulphate was equivalent to 38.1 cc. of decinormal thiosulphate solution, while that from the flask containing manganous sulphate required only 0.5 cc. The aspiration of air was carried on for two hours in the case of the first solution, and two and a-half hours in the case of the second. This might enable a mental picture to be formed of the part played by the manganous sulphate in the Zimmermann-Reinhardt reagent.

Mr. CHAPMAN said that palladium-hydrogen was preferable to stannous chloride as a reducing agent. One of its advantages was that nothing was introduced to interfere with the indicator. The initial expense of the palladium was certainly somewhat large, but not so large as to be of really serious moment.

The CHAIRMAN (Mr. RICHMOND) remarked that it seemed clear, from the work of the authors and of Mr. Birch, that what happened when ferrous solutions were titrated with permanganate in presence of hydrochloric acid was that, while some of the permanganate was used up in oxidising the iron, a portion of it also was used in oxidising some of the oxides of manganese, to form higher oxides, which then formed unstable chlorides, and the speed of the former reaction was greater than that of the latter. That being so, the precaution which the authors recommended of adding the permanganate drop by drop, so as to keep the concentration of the permanganate in all parts of the solution very low indeed, was obviously a wise one. He thought that the difficulty of using bichromate was not so great as had been suggested, especially if the titration was made by artificial light, a practice which he personally much preferred.

A REVISION OF THE ATOMIC WEIGHT OF CHROMIUM.*

FIRST PAPER.—THE ANALYSIS OF SILVER CHROMATE.

By GREGORY PAUL BAXTER, EDWARD MUELLER,
and MURRAY ARNOLD HINES.

Introduction.

THE accompanying table (Clarke, "A Re-calculation of the Atomic Weights," Smithsonian Misc. Coll., 1897) gives the results of investigations upon the atomic weight of chromium from the time of Berzelius, re-calculated with the use of recent atomic weight ratios upon the basis of silver (107.88) and oxygen (16.000). (The following atomic weights are used in the re-calculation of the older values:—Ag = 107.88, Cl = 35.457, Pb = 207.09, N = 14.01, Ba = 137.37, S = 32.07, H = 1.008, K = 39.095, As = 74.96, I = 126.92. The values of Rawson and Meineke are reduced to the vacuum standard, the others are not so corrected).

The value chosen by the International Atomic Weight Committee, 52.1, which is based chiefly upon the more recent determinations, seems to be fairly close to the truth, with an uncertainty of one-tenth of a unit.

It has been repeatedly shown, especially in this laboratory, that most of the earlier work upon atomic weights has been vitiated by neglect of certain fundamental precautions. The incomplete drying of solids has been

* Contributions from the Chemical Laboratory of Harvard College. From the *Journal of the American Chemical Society*, xxxi., No. 5.

Ratio determined.	Atomic weight.
1818—Berzelius (<i>Pogg. Ann.</i> , 1826, viii., 22).	
Pb(NO ₃) ₂ : PbCrO ₄	55.95
1844—Peligot (<i>Ann. Chim. Phys.</i> , 1844, [3], xii., 530).	
CrCl ₂ : 2AgCl	52.33
2CrCl ₂ : Cr ₂ O ₃	51.58
4AgCl: Cr ₂ O ₃	51.61
1846—Berzelius (<i>Berzelius' Jahresberichte</i> , 1846, xxv., 46).	
BaCrO ₄ : BaSO ₄	51.5
1846—Berlin (<i>Fourn. Prakt. Chem.</i> , 1846, xxxvii., 509; xxxviii., 149).	
Ag ₂ CrO ₄ : 2AgCl	52.65
2Ag ₂ CrO ₄ : Cr ₂ O ₃	52.41
Cr ₂ O ₃ : 4AgCl	52.46
Ag ₂ Cr ₂ O ₇ : 2AgCl	52.11
Ag ₂ Cr ₂ O ₇ : Cr ₂ O ₃	52.34
1848—Moberg (<i>Fourn. Prakt. Chem.</i> , 1848, xliii., 114).	
Cr ₂ (SO ₄) ₃ : Cr ₂ O ₃	53.42
(NH ₄) ₂ Cr ₂ (SO ₄) ₄ : 24H ₂ O: Cr ₂ O ₃	53.46
1850—Lefort (<i>Fourn. Prakt. Chem.</i> , 1850, li., 261).	
BaCrO ₄ : BaSO ₄	53.04
1853—Wildenstein (<i>Fourn. Prakt. Chem.</i> , 1853, lix., 27).	
BaCl ₂ : BaCrO ₄	53.56
1855—Kessler (<i>Pogg. Ann.</i> , 1855, xcv., 208).	
K ₂ Cr ₂ O ₇ : KClO ₃	52.23
1861—Kessler (<i>Pogg. Ann.</i> , 1861, cxiii., 137).	
K ₂ Cr ₂ O ₇ : KClO ₃	52.32
2K ₂ Cr ₂ O ₇ : 3As ₂ O ₃	51.92
1861—Siewert (<i>Zeit. gesammte Naturwissenschaften</i> , 1861, viii., 530).	
CrCl ₃ : 3AgCl	52.05
Ag ₂ Cr ₂ O ₇ : 2AgCl	52.14
Cr ₂ O ₃ : 4AgCl	52.04
Cr ₂ O ₃ : Ag ₂ Cr ₂ O ₇	52.05
1884—Baubigny (<i>Comptes Rendus</i> , 1884, xcvi., 146).	
Cr ₂ (SO ₄) ₃ : Cr ₂ O ₃	52.13
1889—Rawson (<i>Fourn. Chem. Soc.</i> , 1889, Iv., 213).	
(NH ₄) ₂ Cr ₂ O ₇ : Cr ₂ O ₃	52.09
1890—Meineke (<i>Liebig's Ann.</i> , 1890, cclxi., 339).	
(NH ₄) ₂ Cr ₂ O ₇ : Cr ₂ O ₃	52.11
2Ag ₂ CrO ₄ : Cr ₂ O ₃	52.10
Ag ₂ CrO ₄ : 2AgCl	52.03
4AgCl: Cr ₂ O ₃	52.14
2Ag ₂ CrO ₄ : NH ₃ : Cr ₂ O ₃	52.27
Ag ₂ CrO ₄ : NH ₃ : 2AgCl	51.62
4AgCl: Cr ₂ O ₃	52.14
Ag ₂ CrO ₄ : 3I	52.41
Ag ₂ CrO ₄ : NH ₃ : 3I	52.05
K ₂ Cr ₂ O ₇ : KHIO ₃	52.14
(NH ₄) ₂ Cr ₂ O ₇ : KHIO ₃	52.13

responsible for many of the discrepancies and errors which exist. Neglect of the solubility of precipitates, together with the use of too concentrated solutions during precipitation, so that perceptible inclusion and occlusion took place, undoubtedly have influenced many gravimetric processes. Volumetric processes have been affected by inaccurately prepared standard solutions, as well as the difficulty inherent in measuring exactly large volumes of solution.

In discussing in detail the applications of the above causes of constant error to the individual investigations, at the best it is only possible merely to indicate the nature of the difficulties; as a rule it is impossible to estimate the

magnitude of the error without repetition of the experimental work. Hence in this paper attention is called only to points in the earlier work which have been experimentally investigated. The uncertainty in most of the previous determinations is emphasised by the lack of agreement in the individual analyses in each series, as well as in the different series.

The choice of method for this investigation was influenced by several considerations. In the first place, the substance to be analysed must be definite in composition, and capable of being either fused or heated to a high temperature in order to ensure the elimination of moisture. In the second place, in view of the fact that chromium is hard to handle satisfactorily in a quantitative fashion, the analytical operation should involve the determination of some other element. The halogen compounds, which have been employed very successfully many times, especially in this laboratory, for the determination of the atomic weights of metallic elements, are less suited for use in the case of chromium on account of the difficulty in the complete precipitation of the halogens by means of silver nitrate. All things considered, the chromates of silver seemed to offer the most promising possibilities on account of the ease with which their silver content may be determined. It is true, in order to determine the ratio of the atomic weight of chromium to that of either silver or oxygen, this method necessitates a knowledge of the exact ratio of the atomic weights of silver and oxygen, knowledge which is at present lacking. The per cent of silver in the compound being known, however, the analytical data may be used at any subsequent time for the calculation of the atomic weight of chromium. Furthermore, since the value for the atomic weight of chromium at present accepted depends very largely upon the analysis of silver chromate, a study of this salt with the application of the most modern methods seemed to promise interesting results, and therefore was first taken up. In the following paper is given a description of the analysis of silver dichromate.

Purification of Materials.

Water.—The laboratory re-distilled water was twice distilled, once from alkaline permanganate, and once from very dilute sulphuric acid. In both distillations, block-tin condensers were employed, no cork or rubber connections being necessary.

Silver Nitrate.—The preparation of pure neutral silver nitrate for the precipitation of silver chromate followed the lines laid down in previous researches in this laboratory. A large quantity of heterogeneous silver residues were reduced to metallic silver by means of sticks of pure zinc in slightly acid solution. After the silver had been washed with water until free from halogens, it was dissolved in nitric acid, and the solution was filtered. Silver chloride was precipitated from the diluted nitrate by means of hydrochloric acid, and the precipitate of silver chloride was thoroughly washed. From this silver chloride, metallic silver was again obtained by reduction with cane-sugar in strongly alkaline solution. After being washed until free from chloride, the metal was again dissolved in nitric acid in a Jena glass flask. By reduction with ammoniac formate (prepared from re-distilled formic acid and re-distilled ammonia), the silver was once more obtained in metallic state. The beautiful mass of crystals was then dissolved in the purest nitric acid, and the nitrate after concentration of the solution was four times re-crystallised from the purest water in platinum until free from acid. In this crystallisation, and in all others, centrifugal drainage in a machine employing platinum funnels as baskets was always used (Richards, *Fourn. Am. Chem. Soc.*, 1905, xxvii., 110), in order to free the crystals entirely from any adhering mother-liquor, the mother-liquors always being rejected.

Hydrochloric Acid.—Hydrochloric acid was prepared by distilling the commercial chemically pure acid, after dilution with an equal volume of water.

Hydrobromic Acid.—The methods for obtaining pure bromine have been recently tested by one of us (Baxter, *Journ. Am. Chem. Soc.*, 1906, xxviii., 1322). The processes found suitable for the purpose were employed here. A considerable quantity of hydrobromic acid was prepared by passing a current of pure washed hydrogen sulphide through a layer of bromine covered with water. After the precipitated mixture of sulphur bromide and sulphur had been removed by decantation and filtration, the acid was boiled, with the occasional addition of small portions of re-crystallised potassium permanganate. This was done to eliminate any iodine which might have been present. The hydrobromic acid was then heated with the calculated quantity of re-crystallised potassium permanganate, the bromine being condensed in a Jena flask cooled with running water. The greater part of the chlorine was undoubtedly eliminated by this operation, since the original bromine was fairly pure. In order to be on the safe side, however, the bromine was again reduced to hydrobromic acid, and this in turn was changed to bromine as above. From the product, the final hydrobromic acid was prepared with hydrogen sulphide. After filtration and distillation, it was preserved in Jena glass.

Chromic Acid.—This was prepared from Merck's "Highest Purity Chromic Acid." The material was dissolved in pure water, and the solution was filtered through a Gooch crucible with a mat of platinum sponge, a quantity of sandy material being thus separated. The solution was then evaporated to saturation, and three times systematically re-crystallised in platinum dishes with centrifugal draining, each mother-liquor being used for the crystallisation of three crops of crystals on account of the small temperature coefficient of solubility of chromic acid. The mother-liquors from the first crystallisation, on testing in the nephelometer, indicated only traces of sulphates and halogens.

Potassium Chromate.—Some of the purest commercial salt, after solution in water, was filtered through a Gooch-Munroe-Neubauer crucible. It was then four times crystallised in platinum, each crop of crystals being centrifugally drained.

(To be continued).

NOTICES OF BOOKS.

First Stage Inorganic Chemistry (Practical). Revised Edition by H. W. BAUSOR, M.A. London: W. B. Clive. 1909.

THE practical work described in this book, which belongs to the Organised Science Series, is designed to cover the new syllabus of the First Stage Examination of the Board of Education, and it appears to be well adapted to its purpose. No attempt is made to deal with theory, but the directions for the experiments are concise and definite, leaving little chance for the beginner to misunderstand them. The author is not to blame if the course is not systematic enough to be really suitable as an introduction to general chemical work. The book includes some simple quantitative experiments, such as the determination of water of crystallisation and equivalents, and elementary volumetric work, &c., and although the treatment throughout is very slight the student will become acquainted with simple chemical operations and will acquire a superficial knowledge of the most common reagents employed in inorganic work.

Industries du Plomb et du Mercure. ("The Lead and Mercury Industries"). By A. BOUCHONNET. Vols. I. and II. Paris: Octave Doin et Fils. 1909.

THE Scientific Encyclopædia of which these two volumes form a part is to include some 1000 monographs, com-

bining the advantages of a dictionary of pure and applied science with those of the most comprehensive treatises on the various subjects. The monographs are intended not so much as text-books for students as for the use of specialists in the different branches, and the list of authors gives promise of really valuable works. The price of each monograph is fixed at a by no means large sum, and they are of convenient size for constant use. These two volumes deal with the mercury and lead industries. In the first the metallurgy of the metals is discussed. The descriptions of plant and furnaces are brief when compared with those contained in the larger treatises on metallurgy, but the processes chosen for notice are in all cases typical and the omissions are on the whole judicious. Methods of analysis of the metals are shortly treated at the end of the book. The second volume, which follows the same plan as the first, deals with the compounds of the two metals, their manufacture, and methods of analysing them for probable impurities. All compounds which are of importance industrially or in therapeutics are included, and many ways of preparing each are described.

Einrichtung von Laboratorien. ("The Arrangement of Laboratories"). By Dr. VICTOR SAMTER. Halle-a.-S.: Wilhelm Knapp. 1909.

THIS monograph contains very useful advice of a most practical nature designed to help the chemist, who, after training in a well-equipped laboratory attached to a large institution, finds himself set down to work under far less favourable conditions in a smaller laboratory which is without many of the appliances which he has been in the habit of using, and which he regards as indispensable. The book has been written more particularly for the analytical chemist, and describes the best arrangement of the laboratory when the space for disposal is somewhat limited, and has to be put to the best possible use. Some of the hints will perhaps necessarily be regarded as counsels of perfection, but at any rate they are some guide in the equipment of a new, or the alteration of an old, laboratory. The most useful forms of apparatus for all purposes are shortly described and illustrated, and the best kinds of balances, stills, graduated vessels, &c., are enumerated, taking into account particularly the fact that the chemist will not have an unlimited number of them. The cost of equipment is always kept in view, but at the same time it is remembered that economy of time and money are not always compatible, and some labour or time-saving appliances are well worth even comparatively high prices. The monograph should certainly be added to the library of the young chemist whose course of training is just completed, and, whatever his career is to be, he will find that it contains many useful hints.

Scientific Exhibition at Westminster.—The Mode Engineering Exhibition which opens at the Royal Horticultural Hall, Westminster, S.W. on Friday, October 15th, will contain some exceptionally interesting exhibits. There will be a number of model aeroplanes on view, including the machine designed by Mr. G. P. Smith which won the gold medal in the recent contest at Wembley Park. Working model steam and electric railways, electric clocks, light machine tools, model motor boats, a model engineers' workshop in operation, and a working demonstration of wireless telegraphy by the latest Marconi apparatus, are some of the numerous attractions which will be presented; while in the competitions for engineering and electrical model making, over a hundred entries have been received. The Exhibition will remain open for eight days, from 12 noon till 10 p.m., closing on Saturday, October 23rd.

CORRESPONDENCE.

EMPLOYMENT REGISTERS.

To the Editor of the Chemical News.

SIR,—I notice in the CHEMICAL NEWS of September 24 (vol. c., p. 159) that the University of London have opened an employment register. While there is much to be said in favour of some such registration, unless it is undertaken by some central body it is likely to do more harm than good.

I would suggest that the various societies, universities, and technical schools should subscribe to a fund to engage a permanent secretary with suitable offices in London. Every member of the subscribing bodies should be enabled to avail themselves of the Employment Bureau; other chemists would have to pay a small yearly registration fee to cover expenses.

The qualifications and experience of each chemist would be known, and employers would know where to write for suitable men. At the same time it would be as well to fix a minimum salary, below which no chemist would work, according to the employment.

The salaries offered by some employers are little better than they pay a skilled labourer. The cause of this is not difficult to discover; there are practising analysts who work at ridiculously small fees. The following examples may interest your readers, and throw some light on why chemistry is a badly-paid profession:—

■ Copper assays at 1s. 3d. each; complete white metal analyses at 5s. each; complete steel analyses at 7s. 6d. each. These are not contracts.—I am, &c.,

ERNEST A. LEWIS.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlix., No. 3, July 19, 1909.

Thorium Phosphates.—A. Colani.—A chlorophosphate of thorium of formula $2P_2O_5 \cdot 3ThO_2 \cdot ThCl_4$, and corresponding to the chlorophosphate of uranium, can be prepared by heating thorium metaphosphate and thorium chloride to a fairly high temperature in an atmosphere of carbon dioxide. Thorium bromide, when treated similarly, gives a bromophosphate of different formula, the analysis of which is very troublesome, and does not lead to satisfactory results. Double phosphates of calcium and strontium also exist having the same formulæ as the corresponding compounds of uranium.

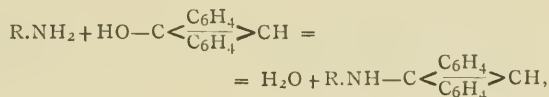
Synthesis of Papaverine.—A. Pictet and A. Gams.—The hydroxyl derivative of homoveratroyl homoveratrylamine, $(CH_3O)_2C_6H_3 \cdot CHOH \cdot CH_2 \cdot NH \cdot CO \cdot CH_2 \cdot C_6H_3(CH_3O)_2$, when subjected to the action of phosphoric anhydride is very readily converted into papaverine. The parent substance can be obtained from veratrol by converting it first into acetoveratrone, $(CH_3O)_2C_6H_3 \cdot CO \cdot CH_3$, then into the chlorhydrate of aminoacetoveratrone, which gives homoveratroyl - aminoacetoveratrone with caustic soda. This compound yields the secondary alcohol homoveratroyl-oxy-homoveratrylamine, $(CH_3O)_2C_6H_3 \cdot CHOH \cdot CH_2 \cdot NH \cdot CO \cdot CH_2 \cdot C_6H_3(CH_3O)_2$, with sodium amalgam in alcoholic solution. This synthesis confirms the constitutional formula which has been given for papaverine.

Catalysis of Acids of Formic Acid Series.—J. B. Senderens.—Certain oxides, e.g., those of thorium and uranium, give a practically theoretical yield of the corre-

sponding symmetrical ketone with pure acetic, propionic, &c., acids. The yields with uranium oxides are less than with thorium, and they seem to lose their activity after a time. Probably the oxides form very unstable compounds which decompose as soon as they are formed, the compounds of uranium and thorium oxides being specially unstable. The reaction has been followed in the case of zinc oxide, and the following equations express what occurs:— $2CH_3CO_2H + ZnO = H_2O + (CH_3CO_2)_2Zn$, $(CH_3CO_2)_2Zn = CH_3 \cdot CO \cdot CH_3 + CO_2 + ZnO$. In the case of zinc and cadmium oxides and lime the destruction of the intermediate salt formed becomes more difficult as the acids used are richer in carbon.

Presence of 2,3-dimethoxy-4,5-methylene-dioxy-1-allylbenzene in Essence of Sea Samphire.—Marcel Delépine.—By fractional distillation under low pressure of essence of sea samphire, *Crithium maritimum*, large quantities of a compound of formula $C_{12}H_{14}O_4$ can be isolated. The reactions of this substance show that it is identical with 2,3-dimethoxy-4,5-methylenedioxy-1-allylbenzene, and that its constitutional formula is $C_6H(OCH_3)_2 \cdot 3(OCH_2)_4 \cdot 5(CH_2 \cdot CH : CH_2)^1$.

Reactions with Anthranol.—Robert Padova.—When heated with phenylchloroform in toluene anthranol gives a small quantity of dianthrone and a good yield of dichlorobenzylanthrone. With arylamines it gives arylanthramines according to the equation—



and with phthalyl chloride in presence of concentrated sulphuric acid it yields phthalylideneanthrone. Anthranol is oxidised by phenanthrenequinone in acetic solution, giving dianthrone. The action of phosphorus pentachloride on anthranol gives a substance fusing at $298-300^\circ$, and containing neither phosphorus nor chlorine. The author is continuing the study of this compound.

Di-iodo Addition Products of Higher Fatty Acids of Series $C_nH_{2n-4}O_2$.—A. Arnaud and S. Posternak.—In acetic acid the fixation of iodine by stearic, behenic, and other acids of the same series is almost instantaneous, and the formation of the di-iodo derivative provides a convenient means of rapidly identifying these unsaturated compounds. Moreover, the presence of an acid of the series $C_nH_{2n-4}O_2$, mixed with fatty acids of other series, can readily be detected by the isolation of the iodo derivative. The authors have prepared the di-iodo derivative of tariric, stearic, and behenic acids, and have observed that in each case the melting-point of the derivative is very close to that of the parent acid. They have analysed the acids, obtaining results which agree well with the theoretical values, and have also investigated the properties of the iodo acids and their salts.

Ergothionine, a New Base obtained from Ergot of Rye.—C. Tanret.—A warm solution of mercuric chloride precipitates a chloromercurate in an alcoholic solution of ergot of rye. This can be decomposed by sulphuretted hydrogen, and from the liquid the chlorhydrate of ergothionine crystallises. It may be decomposed by sulphuric acid, the hydrochloric acid set free being removed by ether, while the sulphuric acid is precipitated with barium chloride. The filtrate is distilled under pressure, the residue being ergothionine, the formula of which is $C_9H_{15}N_3O_2S \cdot 2H_2O$. It crystallises in water in colourless lamellæ, and is very soluble in hot water, fairly soluble in weak alcohol, and only very slightly soluble in strong alcohol. It is dextrorotatory, $[\alpha]_D^{20} = +110^\circ$. It is not volatile. It is a feeble base, without action on litmus. Its salts with acids have the peculiar property of acting on indicators as if the acid were free. It reacts with hydrochloric and sulphuric acids like a monacid base.

Constitution of Perseulose.—Gabriel Bertrand.—The oxidation of perseite by the bacteria of sorbose gives a new reducing sugar, perseulose, the formula of which is $C_7H_{14}O_7$. This sugar is a ketonic sugar, for it is not oxidised by bromine in aqueous solution, and, moreover, when hydrogenated by means of sodium amalgam and water it gives a mixture of two stereoisomeric alcohols, one of which is perseite, while the other, which has not been prepared previously, may be called perseulite. This result can only be explained on the assumption that perseulose contains the CO group in its molecule. Its relation to perseite is exactly the same as that of sorbose to sorbite, and it is thus the first representative of ketonic sugars with 7 atoms of carbon.

No. 4, July 26, 1909.

Decomposition of Water by Ultra-violet Rays.—Mirosław Kernbaum.—The ultra-violet light from a mercury lamp sets free hydrogen from water, and simultaneously forms hydrogen peroxide, and this fact explains the sterilisation of water by ultra-violet rays. It also explains the observations of Schöne that hydrogen peroxide is found in rain and snow, that the quantity of it is greater in the day than at night, and that there is none in dew.

Liberation of Radium Emanation.—H. Herchfinkel.—The liberation of radium emanation can be greatly facilitated by diluting the radium with the rare earths, which set free the emanations of thorium and actinium. Using the hydrates of didymium, iron, uranium, thorium, aluminium, barium, the fluorides and oxalates of barium and didymium, chromates of barium and iron, sulphates of barium and lead, and determining the emanation set free, the author has shown that the hydrates of iron and aluminium carry down nearly all the radium, while the other hydrates only carry down very little. All the hydrates set free a fairly large proportion of emanation in the dry state. The amount liberated by salts of barium is very small, and does not usually depend on the nature of the radical. Didymium fluoride and iron chromate set free a large proportion, didymium oxalate less, and lead sulphate still less.

Allotropic States of Phosphorus.—Pierre Jolibois.—Ordinary red phosphorus, obtained by heating yellow phosphorus, is in an unstable though definite state, and even at the temperature at which it is formed a catalytic agent is sufficient to transform it into a stable variety with a density 9 per cent higher. This modification the author calls pyromorphic phosphorus. It may be obtained by the action of heat alone above 360° , and in presence of a catalyser above 250° . Its density is 2.37. Red phosphorus can be fused by heating it to 725° .

Hydrates of Thorium Bromide and Chloride.—Ed. Chauvenet.—The normal hydrate of thorium chloride, $ThCl_4 \cdot 8H_2O$, is transformed into $ThCl_4 \cdot 4H_2O$ at 50° , and at the same temperature the hydrate of thorium bromide which contains 12 molecules of water, and which is obtained by evaporating $Th(OH)_4$ with HBr, yields $ThOBr_3 \cdot H_2O$. This last compound is analogous to $ThOHCl_3 \cdot H_2O$ which is formed at temperatures above 100° only. At 105° $ThBr_4 \cdot 12H_2O$ yields $ThOBr_2$, and $ThCl_4 \cdot 8H_2O$ yields $ThOCl_2$ at 250° . Thus the oxyhalogen derivatives of the bromide are formed at much lower temperatures than the corresponding derivatives of the chlorides.

Derivatives of 1,2,4-Butanetriol.—M. Pariselle.—The bromide, $CH_2Br \cdot CHBr \cdot CH_2 \cdot CH_2OCH_3$, yields the corresponding glycol, $CH_2OH \cdot CHOH \cdot CH_2 \cdot CH_2OCH_3$, when it is boiled with water, and the liquid is neutralised with lead carbonate and evaporated *in vacuo* after filtration. Oxyhydrofurfuran is also formed. From the glycol 1,4-dibromo-2-butanol can be prepared, and from this the oxide of butylene bromide, $CH_2-CH-CH_2-CH_2Br$

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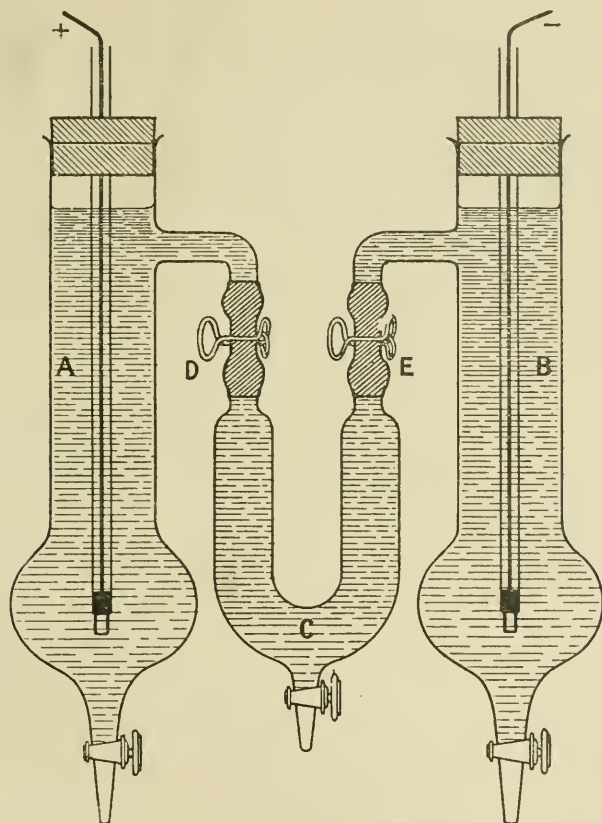
THE CHEMICAL NEWS.

VOL C., No. 2603.

APPARATUS FOR THE DETERMINATION OF TRANSPORT NUMBERS.

By ALEX. FINDLAY, M.A., D.Sc.

FOR the determination of the transport numbers of ions, various forms of apparatus have been devised. The simplest of these, *e.g.*, the familiar H-shaped vessel, suffer somewhat from the defect that they do not allow of sufficiently definite separation for analysis of the anode and intermediate portions of the solution, or are of restricted application; while the more complicated forms are rather costly and somewhat cumbersome in use. For general laboratory practice the form described below has been



found satisfactory. It is simple to use, and can be employed in the case of all solutions.

The apparatus consists of three tubes, all of which are furnished with small glass taps, through which the solution can be run out. The two outer tubes, A and B, in which the electrodes are placed, are connected by a U-tube, C, by means of rubber tubing furnished with spring clips. During the course of the experiment, while the current is passing, these clips are, of course, kept open. At the conclusion of the experiment the spring clips are closed, and the anode liquid is then run off for analysis through the tap at the bottom of the appropriate tube (A) into a weighed flask. This tube and the electrode are washed

with a small quantity of the original solution, which is also run into the same weighed flask. The clip at D is then opened, and the intermediate solution in the U-tube is likewise collected for analysis. If desired, the cathode solution can be run off similarly.

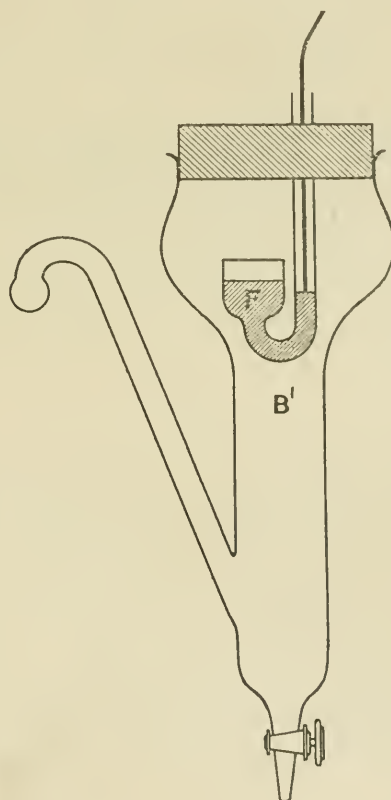
For the determination of transport numbers in those cases where a gas is evolved at the cathode, the tube B of the former apparatus is replaced by B', and a mercury electrode (F) employed as cathode, as in the case of the apparatus due to Hopfgartner.

The University, Birmingham.

THE THERMO-CHEMISTRY OF THE HALOGENS.

By J. C. THOMLINSON, B.Sc.

THE following investigation is intended to establish the existence of thermo-chemical equivalents in connection with the compounds of the halogens, at any rate theoretically and approximately.



By thermo-chemical equivalent I mean the amount of heat which is associated with a chemical equivalent of any element and given out or absorbed during reaction.

A preliminary consideration of a few simple compounds will enable us to form a conception of these thermo-chemical equivalents as used in connection with the study of the halogens, and also of the change of equivalence with the valency value of the elements.

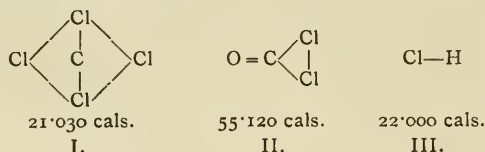
In the first place I will merely state the heats of formation of methane, carbon dioxide, and water to be 21.750 cals., 96.960 cals., and 68.361 cals. respectively, and that simple algebra gives the following equivalents in calories for atomic weights in grms. :—

		In former numbers of the CHEMICAL NEWS (a).
H	=	7·689
O	=	52·983
C	=	-9·005
		7·470
		52·545
		-8·140

(a) These were the numbers I used for the equivalents of hydrogen oxygen and carbon when first dealing with the subject in the *CHEMICAL NEWS*.

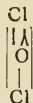
I must refer readers to former numbers of the *CHEMICAL NEWS* for the literature dealing with the establishment of the equivalents for these elements.

Taking chlorine, I propose to consider it as divalent in carbon tetrachloride and oxychloride, and, of course, monovalent in hydrochloric acid, and see how the numbers arrived at for its thermo-chemical equivalent as a divalent and monovalent element are justified when used to form a theoretical value for the heat of formation of chlorine monoxide.



Carbon we found to have a thermo-chemical equivalent -9·005 cal., which, applied in Equation I., gives to divalent chlorine a thermo-chemical equivalent, 7·509 cal. From carbon oxychloride we obtain in a similar way Cl = 5·581 cal., the mean of these values being 6·540 cal. For monovalent chlorine we at once have a value 22·000 - 7·689 = 14·311 cal.

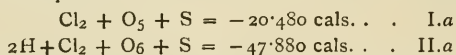
Chlorine monoxide has a very low heat of formation, viz., -17·930 cal., and I propose to consider its chlorine atoms as quadrivalents united with pentavalent oxygen as below:—



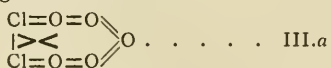
Monovalent chlorine Cl = 14·311 cal., and divalent chlorine —Cl— = 6·540 cal. The difference in equivalents for the valency is equal to 7·771 cal.; hence the difference of two valencies in making quadrivalent chlorine we would expect to be +15·541 cal., and as divalent chlorine is 6·540 cal., the value for quadrivalent chlorine would be -15·541 + 6·540 = -9·001 cal.

This would give us a theoretical value for chlorine monoxide -18·002 + 4·691 = -13·311 cal. as against -17·930 cal. obtained by experiment.

The application of the foregoing to the consideration of the theoretical and calculated heats of formation of chlorine pentoxide and chloric acid involve a consideration of the following equations, in which S represents the heat of solution of the compound:—



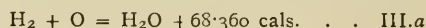
In Equations I.a and II.a one is led from a knowledge of chemical reactions to say that the same reactions take place, chloric acid being formed in both cases.



(NOTE.— $\text{O}\equiv$ = -4·691 cal.; $\text{O}\equiv$ = 19·225 cal.; $\text{O}\equiv$ = 52·983).

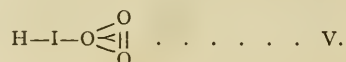
The structural Formula III.a gives a heat of formation for this compound approximately 28·000 cal.; hence the heat of solution of chlorine pentoxide is equal, approximately, -48·000 cal., and a confirmation of this heat of

solution is found in Equation II.a, where chlorine pentoxide is formed, and goes into solution with absorption of 47·880 cal., taking about 20·000 cal. from the elements of water which enter into the reaction, and making the heat of formation of chloric acid in water +68·000 - 20·000 = 48·000 cal. (approximately), that by theory being 47·880 cal.



When we come to consider iodine we find hydrogen iodide, HI = -6·040 cal., gives us a thermo-chemical equivalent for monovalent iodine, I = -17·729 cal.

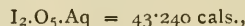
From analogy I give iodine pentoxide the formula in Figure IV., whence the thermo-chemical equivalent of quadrivalent iodine = -1·632 cal.



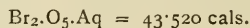
Iodic acid, regarding its structure as above, Figure V. involves divalent iodine which by reference to mono- and quadrivalent values for this element should have a thermo-chemical equivalent equal to -5·120 cal., giving a calculated heat of formation, 7·689 - 5·120 = 2·569 + 57·675 = 60·244 cal. as against 57·960 cal., the theoretical value.

When we come to deal with bromine we find at once its monovalent value Br = 8·440 cal. - 7·689 cal. = 751 cal., it standing midway between chlorine and iodine with values 14·311 cal. and -13·729 cal. respectively.

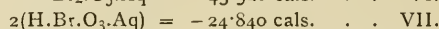
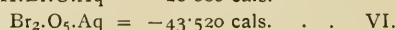
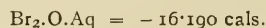
Such an equality on each side of practically zero leads us to immediately consider iodine pentoxide formed in water,—



and bromine pentoxide in a similar way,—



These two compounds are also practically equidistant from zero, and hence if I— = -13·729 cal. and I≡ = -16·32 cal., whilst Br— = 751 cal., we might be inclined to think that Br≡ is approximately also -13·700 cal.



Giving bromine pentoxide a formula and structure similar to chlorine and iodine pentoxides, we would expect the first mentioned compound to have a heat of formation -27·400 + 7·689 + 57·675 = 37·962 cal.

Equations VI. and VII. differ from one another in that the elements of water enter into reaction in Equation VII., otherwise the products of the reaction are the same.

In Equation VI. the heat of solution is -81·484, and in Equation VII. bromine pentoxide is formed, unites with the elements of water, and goes into solution with a calculated heat evolution -81·484 + 68·361 + 37·964 = 24·841 cal., which agrees with the experimental value given.

"Official Chemical Appointments."—The preparation of the Third Edition of "Official Chemical Appointments" is now in hand. Corrections should be forwarded to the Registrar without delay. Suggestions which may increase the usefulness of the List will be carefully considered. All communications to be addressed to the Registrar, Institute of Chemistry, 30, Bloomsbury Square, London, W.C.

SOME RECENT RESULTS OF ASTRONOMICAL RESEARCH.*

By ARTHUR STANLEY EDDINGTON, M.A., M.Sc., F.R.A.S.,
Chief Assistant in the Royal Observatory, Greenwich.

THE object of this discourse is to give some account of two or three of the principal points of interest that have come before astronomers during the past year. It has seemed preferable to concentrate attention on a few points rather than to make any survey of the general progress of astronomy, and I have naturally selected that work with which the Royal Observatory, Greenwich, was most concerned, and which can best be illustrated with slides. That must be the excuse for neglecting many important results which have been obtained along other branches of the subject.

The Eighth Satellite of Jupiter.

The first result of which I have to speak is the discovery of an eighth satellite of Jupiter. This body was discovered by Mr. Melotte at the Royal Observatory, Greenwich, on February 28 last year. (A slide was shown of part of the photograph on which the new satellite was found). If there are any here who are quite unfamiliar with celestial photographs, I may explain that when a photograph is being taken of any object such as a planet or satellite which is moving relatively to the stars, it is necessary to keep the telescope pointing continually on the object, making proper allowance for its motion, the stars being, as it were, left to take care of themselves. The result is that the stars make little streaks on the plate. You see these scattered about everywhere. Now, in this case the plate was made to follow the motion of the planet Jupiter during an exposure which lasted an hour and twenty minutes, and among these streaks or trails were found three round images, which evidently belonged to objects moving at nearly the same rate as Jupiter, and thus distinguished themselves from the fixed stars. It may be mentioned, however, that they do not distinguish themselves from photographic defects so readily. Two of the three images were of the objects for which the photograph was taken, namely, the sixth and seventh satellites of Jupiter discovered by Perrine at the Lick Observatory, California, in the winter of 1904-5. Since then it has been our practice at Greenwich to photograph them at frequent intervals, for the study of their motions presents many points of astronomical interest; the seventh satellite in particular is very faint and requires powerful instruments, long exposure, and, may we add, a favourable climate for its observation. The third round speck was something new, which could not have been expected; it was an eighth satellite of Jupiter.

But it was a long while before its real nature could be determined definitely, though it was suspected from the very first. Just previous to its discovery, a number of plates of the sixth and seventh satellites had been taken, and by looking back at these, Melotte was able to trace the new object on seven of them. Thus there could be no doubt that it was a real body and not a defect of the plate. The fact that it moved along at almost the same rate with Jupiter was suspicious, but still it was by no means certain that it belonged to Jupiter; it might only be a new comet, or, still worse—a new minor planet, one of the "small vermin of the heavens." One thing, however, was quickly established; Mr. Crommelin calculated that, whether it belonged to Jupiter or not, it was at all events near Jupiter, and not merely in the same line of sight. That in itself was sufficient to make it an interesting body. I cannot give you any idea of the calculations which ultimately showed that it belonged permanently to Jupiter; perhaps the next slide will show that the hesitancy in coming to a definite decision as to its real nature was not unjustified; it may even seem somewhat daring to have acknowledged it as probable. (The slide showed the observations of the three outer satellites made at Greenwich during the oppo-

sition of 1908). There is no difficulty in seeing VI. and VII. belong to Jupiter, they are clearly circulating round it; but the eighth satellite looks, at first sight, to be going on its way regardless of Jupiter. Its path is apparently convex to the planet instead of concave to it as would be expected. It is not easy to see how it will get round it at all. That difficulty, however, disappears when the change of position of the Earth and Jupiter, altering the point of view from day to day, is taken into account. The record of the diagram breaks off in April; after that Jupiter became unfavourably placed for observation, and the satellite could only be followed by calculation through its course during the summer and autumn. At the first opportunity, however, it was searched for, and in January it was found again at Greenwich, very near to the predicted spot. (One of this year's photographs was thrown on the screen). It has now moved far away from Jupiter, which no longer comes on to the plate; but it is still and will be under the control of the giant planet, and we can say as confidently as in the case of the other satellites, that it is really circling round Jupiter.

The satellites of Jupiter now form a very remarkable family, and before we go on to say more about the new satellite it seems worth while to consider this system a little in order to appreciate the importance of the latest addition. (A diagram of the system was shown). Of the first four satellites not much need be said; their discovery by Galileo in 1610 was one of the first-fruits of the invention of the telescope. It was to the study of their eclipses that we owe one of the most epoch-making of all scientific discoveries, the discovery that light moves with a finite speed and not instantaneously; and lest it should be supposed that they are now only of historic importance, I may add that it has recently been suggested that it may be possible ultimately to determine by their aid that extraordinarily elusive quantity the motion of the aether relative to the sun. (It would seem, however, to be impossible to separate this quantity mathematically from the eccentricities of the orbits of the satellites, so that it is unlikely that a determination can be made in this way). In actual size these four satellites are quite considerable, being, in fact, larger than our moon. For 380 years these were all that were known, and the remaining four that have been found in quite recent times are very faint and minute objects. One hesitates to give an estimate of their actual sizes, but, at a rough guess, probably Satellites VII. and VIII. are globes about twenty-five to thirty miles in diameter. No. V. was discovered by Barnard in 1892, and is remarkable for its closeness to the planet. It takes barely twelve hours to go round, and as Jupiter rotates once in about ten hours the satellite nearly keeps up with the planet. VI. and VII. are a curious pair. The order and regularity which seemed to characterise Jupiter's system is now quite disobeyed. There is a great gap separating them from the inner satellites. Their orbits are very nearly equal in size; in fact, No. VI. takes about 250 days to revolve, and No. VII. only seven days longer. The orbits are both inclined at 30° to the plane of the ecliptic, but in different directions, so that they do not intersect, and there is no fear of a collision. The orbits are actually interlocked.

The natural place where one might expect to find new satellites of Jupiter, and where, perhaps, new satellites may yet be discovered, would be in the great gap which intervenes between the inner satellites and these two; but the eighth satellite was actually far outside them all. Its orbit also is inclined 30° to the ecliptic. No. VIII. is altogether a record-breaking satellite. When at the farthest point of its orbit it is 21,000,000 miles from Jupiter, a distance suggesting rather the interval between one planet and another than between an ordinary satellite and its primary. Venus sometimes approaches the Earth within a distance not much greater than this, and the minor planet Eros occasionally comes very much nearer to us. The satellite will take more than two years to go round the orbit. (A recent paper by Cowell, Crommelin, and Davidson shows that the orbit is so far from being a closed

* A Discourse delivered before the Royal Institution, March 26, 1909.

curve that it is almost meaningless to speak of a definite "period" of the satellite).

Jupiter's year, or time it takes to go round the sun, is equal to nearly twelve of ours. The satellite's "month," or time it takes to go round Jupiter, is somewhat over two of our years. It follows that the satellite goes rather more than five times round Jupiter whilst Jupiter goes once round the sun. We may say that for J VIII. there are five months in the year, borrowing terminology of the Earth-Moon system. Now this is a record. All the other satellites in the solar system have a much greater number of "months" to the "year," usually several hundreds, sometimes even thousands. Our own moon previously held the record with between twelve and thirteen months to the year, but the new satellite far outdoes that. Now this is a particularly interesting piece of record breaking, because the number of satellite's months in the planet's year expresses, generally speaking, the proportionate share which the planet and sun have in controlling the motion. When, as is usually the case, the number is several hundreds, that means that the share of the planet is far greater than that of the sun, and the orbital motion is easy to compute; in the case of our Moon, which, as I have said previously, held the record, the disturbance by the sun is considerable, and the prediction of the motion is a very complicated problem; but when, as in the case of J VIII., the number gets nearly down to five, ordinary methods of calculation fail altogether, and when Mr. Cowell attacked the problem, he had to devise an entirely new procedure for his purpose.

These four newer satellites of Jupiter thus form a remarkably varied group, each individual presenting its own particular problems. It is hard to say which could least be spared, whether the fifth satellite circling so closely and so rapidly; or VI. and VII., the twins, with their curiously interlocked orbits; or the eighth, which moves at a distance from the planet so great that at first it could hardly be credited.

There is one circumstance, however, which renders J VIII. the most immediately interesting of all—it goes round Jupiter backwards. All the other seven go round in one direction; Jupiter himself rotates in the same direction; but the eighth satellite moves round the opposite way. This is a most significant fact; if we are right in our interpretation, it is a clue which reveals a curious chapter in the past history of the solar system. The speculation which it opens out is not a new one, but this fact gives a strong confirmation to what must previously have been regarded as a plausible but daring hypothesis. In 1899 Phœbe, the ninth satellite of Saturn, was discovered, and after considerably puzzling its discoverer, Professor W. H. Pickering, by its unaccountable motion, was at last found by him to have a retrograde motion; that is, to go round Saturn in the opposite direction to his other satellites, just as we now find J VIII. behaves. Phœbe is a long way the outermost of Saturn's satellites, just as J VIII. is the outermost of Jupiter's. Pickering, of course, had only the case of Phœbe to account for, but he suggested an explanation which is known as the theory of planetary inversion, and which now receives strong confirmation from the discovery of an outer retrograde satellite attending Jupiter.

On this theory it is supposed that each planet, when it separated from the original nebula, or whatever may have been the material from which the solar system was evolved, had originally a retrograde rotation, *i.e.*, a rotation from east to west, or in the opposite direction to the motion round the sun. The motions of Phœbe, and we may now add that of J VIII., are relics of this original retrograde motion, Jupiter and Saturn having now turned right over so as to spin in the forward direction, and all their inner satellites having turned over along with the planets, or else only having detached themselves after the parent planets had turned over. Similarly the Earth and Mars must have turned over, for they are now rotating forwards. In the case of the two outermost planets of our system, Uranus and Neptune, although we do not know their direction of rotation, the motions of their satellites lend

some support to the idea of an original retrograde direction. Still, until the discovery of J VIII., the evidence for the hypothesis rested very largely on Phœbe alone.

How then has it come about that the traces of this original rotation, believed once to have been universal, are so few? The cause suggested is tidal influence. Ever since Sir George Darwin published his classical researches on the Tides, which showed what a remarkable influence tidal effects have exerted in the formation especially of the Earth-Moon system, their importance in all evolutionary processes has become more and more recognised. It is possible that there may be a tendency to press the hypothesis too much now-a-days; the theory is to this extent speculative, that we have very little direct evidence as to the magnitude of the tidal forces, or how many million years are required to produce the effects that are assigned to them. But the effects, though certainly small, are steadily cumulative, so that, granted sufficient time, and there seems no reason why time should be denied, these theoretical results must be brought about.

The results of the action of tidal forces are too complicated for us to do more than touch generally on. The tides raised by the sun and each satellite have each to be considered, and then the attractions of the sun and satellites on their own and each other's tides. The viscosity of the planet is also an important factor. So many particular cases arise that it seems necessary to consider every planet and satellite separately. The mathematics have been worked out in considerable detail by Mr. Stratton, who concludes that tidal action appears to be adequate to explain the characteristics of the various systems of satellites attending on the planets. The mode in which tidal action reverses the direction of the rotation is by tilting over the axis. If you turn a planet over so that what was formerly the north end becomes the south end, this is equivalent to reversing the direction of rotation; the transition from direct to retrograde motion is thus a perfectly gradual one; the satellites of Uranus, in fact, illustrate the intermediate stage; they may be said to move neither backwards nor forwards but sideways. Briefly speaking the effect of the sun, and the tides on the planet raised by the sun, would be to tilt over the planet until its axis was in the plane of its orbit—the intermediate position I have just mentioned.

In the case of a very viscous planet the tilting may proceed still further until, in some cases, the planet goes almost completely over; that is what seems to have happened in the case of Mars and the Earth. The Moon appears to have split off from the Earth after this somersault had been performed, and to have had no share in helping it. But in the case of the other planets, the satellites have had a large share in driving the plane of the planet's rotation right over. Thus Jupiter was tilted rather more than half way by the action of the solar tides, and then he evolved the inner satellites, and it was by their influence that the inversion was completed. Neptune, on the other hand, being very remote from the sun, began to turn over slowly; before the process had gone very far, the satellite was evolved and the plane of rotation began to sink back again to the original position; thus the motion and direction of rotation remain retrograde.

As to what happens to the satellites when the planet turns over, it is almost more difficult to make a generalisation. In some cases the circumstances are such that a satellite, which separated from the planet when it was rotating backwards, would follow the planet's equator and turn over with it. Probably this is what happened in the case of Iapetus and of J VI. and VII. But in other cases, namely, those of Phœbe and J VIII., the satellites are left to retain their original motion.

We see now why it is only the extreme outermost satellites in these two systems that move backwards. They were the earliest to split off and refer to a time before the tilting of the planet by the solar tides had proceeded very far. When the theory was put forward it was predicted that should any very distant satellites of Jupiter and Saturn

be found, they also should revolve backwards. An opportunity for testing this seemed soon to occur. The sixth and seventh satellites of Jupiter were found far outside those previously known; when, therefore, it was found that they moved forwards, the hypothesis received something of a set back. However, it has turned out that these two satellites were not distant enough from Jupiter; the still more remote J VIII. moves backwards and greatly strengthens the theory.

(To be continued).

A REVISION OF THE ATOMIC WEIGHT OF CHROMIUM.*

FIRST PAPER.—THE ANALYSIS OF SILVER CHROMATE.

By GREGORY PAUL BAXTER, EDWARD MUELLER,
and MURRAY ARNOLD HINES.

(Continued from p. 182).

Silver Chromate.—The point in the investigation requiring the most attention was the preparation of normal silver chromate free from both basic and acid salts. Since the salt cannot be crystallised, owing to its slight solubility in water, it is necessary so to regulate the conditions during the precipitation that neither acid nor basic salts can separate as a distinct solid phase. Even then the occlusion of traces of either basic or acid salts is still possible, and it is necessary to form the salt under a fairly wide range of conditions in order to show constancy of composition.

Fortunately data are available which indicate the conditions under which silver dichromate or hydrochromate can exist. Sherrill (*Journ. Am. Chem. Soc.*, 1907, xxix., 1673) has recently shown that silver chromate changes into silver dichromate rapidly under a saturated solution in nitric acid more concentrated than 0.075 normal, while silver dichromate changes into silver chromate under a saturated solution in nitric acid less concentrated than 0.06 normal. Some time before, Krüss had shown that silver dichromate is converted into silver chromate by contact with water (*Ber.*, 1889, xxii., 2030).

In the light of these facts it is obvious that the solutions of the soluble chromates can safely be employed for the precipitation of silver chromate without the least danger of the precipitation of silver dichromate, and even that the presence of a slight amount of free acid could do no harm.

Owing to the weak nature of the second hydrogen of chromic acid, the first hydrogen dissociating to the same extent as that of hydrochloric acid (Walden, *Zeit. Phys. Chem.*, 1888, ii., 49), but the second hydrogen having the constant 6.0×10^{-7} at 18° (Sherrill, *loc. cit.*), appreciable hydrolysis of solutions of its salts takes place, to a greater extent the weaker the base with which the chromic acid is combined. Sherrill has found, for instance, that ammonium chromate in 0.05 molar solution is 2.7 per cent hydrolysed. The basicity of the solutions, on the other hand, will be greater the stronger the base. In order to determine whether this hydrolysis is sufficient to produce precipitation or occlusion of basic chromates, precipitates of silver chromate were formed by means of solutions of both ammonium and potassium chromates. The comparison of precipitates formed in this way will show whether the presence of basic salts is to be feared.

Sample I.—Ammonium chromate was prepared by adding to a solution of the pure chromic acid a slight deficiency of the purest freshly distilled ammonia. The solution was diluted until about tenth normal, and was slowly poured with constant shaking into a solution of an equivalent quantity of silver nitrate of about the same concentration. The dark red precipitate of silver chromate was washed six times by decantation with large portions of water, centri-

fugally drained to remove as much water as possible, and dried at gradually increasing temperatures in an electric oven, finally at 160° for a long time. The dried lumps were then gently ground to a fine powder in an agate mortar in order to facilitate further drying as well as to ensure homogeneity.

During the addition of the chromate to the silver solution, since the chromate solution was slightly deficient in ammonia, acid accumulated in the silver nitrate solution. Hence each succeeding portion of precipitate was formed under conditions of greater acidity, although the concentration of acid in the solution could never have approached that found by Sherrill to be necessary for the existence of the silver dichromate.

Sample II.—This preparation was practically identical with Sample I., since part of the precipitate obtained as above was washed by decantation with water eight times more, each wash-water being allowed to stand in contact with the precipitate for many hours, and the precipitate being shaken with the wash-water very thoroughly at intervals, in order to leach out any accidentally enclosed or adsorbed soluble salts. The prolonged extra washing evidently was unnecessary, since the results with this sample are practically the same as those obtained with Sample I.

Sample III.—This sample was prepared from the four times re-crystallised potassium chromate. A quantity of this material in about tenth normal solution was precipitated with an equivalent amount of silver nitrate, equally dilute. The precipitation took place in Jena glass, the silver solution being slowly poured into the chromate, in order to accentuate the effect of the hydrolysis if possible. It will be recalled that in the case of Samples I. and II. prepared with the ammonium salt, the chromate was added to the silver solution. The precipitate was then transferred to the platinum, and washed seven times with the purest water, the chromate being thoroughly agitated with each washing. After the removal of the greater part of the adhering water by centrifugal settling, this sample was dried in a preliminary fashion at 150°, and was pulverised in an agate mortar, as in the case of Samples I. and II. The salt was soft and crystalline, and greenish black in colour.

Sample IV.—A fourth sample also was prepared from re-crystallised potassium chromate, which in turn was made from re-crystallised chromic acid. In the first place, potassium hydroxide was prepared by the electrolysis of three times re-crystallised potassium oxalate, with the use of a mercury cathode and decomposition of the amalgam with pure water in a platinum dish, as in the preparation of potassium hydroxide in an investigation upon the atomic weight of potassium (Richards and Mueller, *Journ. Am. Chem. Soc.*, 1907, xxix., 645). The solution of the pure hydroxide was added to a solution of three times re-crystallised chromic acid, contained in a platinum dish, until the normal chromate had been formed as indicated by the yellow colour. From this solution, by three systematic crystallisations, potassium chromate was separated.

The silver chromate was prepared from this material, and the purest silver nitrate by slowly adding a six hundredth normal solution of the chromate to a silver nitrate solution of equivalent concentration, this procedure being the reverse of that used in the preparation of Sample III. The dark brownish red precipitate was allowed to settle in the flask in which precipitation took place. Then, the supernatant solution having been decanted, the silver chromate was transferred to a platinum dish and washed very thoroughly with water. After being freed from water by centrifugal settling, the silver chromate was dried at about 160° in an electric oven, and powdered in an agate mortar.

Since in the case of Sample III. the silver nitrate was added to the chromate, while in preparing Sample IV. precipitation took place in the reverse fashion, a comparison of the two samples would not only throw light upon the effect of hydrolysis, but also show whether the occlusion of potassium chromate or silver nitrate was to be feared.

* Contributions from the Chemical Laboratory of Harvard College. From the *Journal of the American Chemical Society*, xxxi., No. 5.

The Analysis of Silver Chromate.—The fact that salts dried by prolonged heating at 100°, or at even higher temperatures, usually contain appreciable amounts of moisture, owing to included mother-liquor, is a point which has been overlooked by most earlier investigators (Richards, *Proc. Am. Phil. Soc.*, 1903, xlii., 28), and the oversight throws doubt on much otherwise very careful work. In exact work, the residual water must either be corrected for or entirely avoided. The simplest fashion of drying a substance perfectly is to fuse it in a current of dry gas. In the case of the silver chromate, however, this is not practicable, for even at 300° incipient decomposition sets in. Upon attempting to dissolve in nitric acid samples dried in air at that temperature, a slight insoluble residue was always obtained, while heating in a current of oxygen gave no better results. Since the moisture cannot be entirely expelled from silver chromate by heating at a moderate temperature, it must be determined by the analysis of separate portions of the substance which have been treated in some definite fashion.

Experiments showed that at temperatures below 225° the salt was not appreciably changed, hence this temperature was chosen as a suitable one at which to heat the salt preparatory to analysis. The silver chromate was therefore always heated in a current of pure dry air for two hours at 225°, in order to obtain the separate portions in as nearly as possible the same condition.

The drying apparatus was constructed entirely of glass, rubber connections being especially avoided. A current of air was passed first over red-hot copper oxide to destroy organic matter, then through successive Emmerling washing towers. In the first were beads drenched with silver nitrate solution, in the second with a strong solution of potassium hydroxide containing much potassium manganate, and in the last three with concentrated sulphuric acid. The already very dry air was then passed through a long tube containing re-sublimed phosphoric anhydride spread over a large surface of glass beads and ignited asbestos. From the drying apparatus the air passed into the tube in which the boat containing the silver chromate was placed.

The Determination of Silver in Silver Chromate.—During the drying of the silver chromate it was contained in a platinum boat which had been weighed, in a weighing bottle, by substitution for a similar bottle, which with its contents displaced the same amount of air as the bottle with the boat. The boat was placed in a hard glass tube connected by a carefully ground joint with a bottling apparatus, by means of which the boat could be transferred to the weighing bottle, after being heated, without the slightest exposure to moist air (Richards and Parker, *Proc. Am. Acad.*, 1896, xxxii., 59). The tube was heated by means of two solid aluminium blocks which were grooved to contain the tube, by means of which the temperature could be maintained constant within a very few degrees (Baxter and Tilley, *Journ. Am. Chem. Soc.*, 1909, xxxi., 206). After two hours' heating at 225° the boat was transferred to the weighing bottle, and was allowed to stand in a desiccator near the balance for several hours before being weighed.

Next, the weighed quantity of silver chromate was transferred to a 3-litre glass-stoppered Jena glass flask with a carefully ground stopper, and, after the boat and bottle had been cleaned with hot dilute nitric acid and water, the rinsings were poured into the flask, and the silver chromate dissolved by the application of gentle heat. If the salt had not been heated above 225°, the solution was absolutely clear. Specimens heated above this temperature always showed more or less turbidity.

The chromate was next reduced to the chromic state by the addition of a very slight excess of sulphur dioxide which had been freshly distilled into pure water. The slight excess of sulphurous acid was soon oxidised under the combined influence of heat and nitric acid. In Analyses 1, 2, 3, 12, 13, and 14, the reduction was effected by means of re-crystallised hydrazine sulphate, in order to avoid to a large extent the presence of sulphuric acid, for

Richards and Jones found that silver chloride occludes silver sulphate very tenaciously (*Journ. Am. Chem. Soc.*, 1907, xxix., 831). This method of reduction, however, was without effect on the results.

Since in the reduction of the chromate by hydrazine nitrogen gas is evolved, the flask in which the reduction took place was protected from loss by spattering by means of a long column of bulbs fitting loosely into the neck of the flask. The solution of hydrazine sulphate was added through a funnel with a long fine stem which extended through the column of bulbs nearly to the bottom of the flask. After the addition of the hydrazine, the reaction was allowed to continue slowly, with occasional shaking, and was completed by heating the solution upon a steam-bath for a short time. In the presence of acid a dilute solution of hydrazine is without effect upon silver salts.

After the solution had been allowed to cool, it was diluted to a volume of 1½ litres, and the silver was precipitated as chloride or bromide by the addition of a very dilute solution of an excess of either hydrochloric or hydrobromic acid. The flask with its contents was shaken thoroughly for a few moments, and was then allowed to stand several days, until, the silver bromide having settled, the supernatant solution was perfectly clear.

Since the mother-liquor of the silver halide contained both nitric and hydrobromic acids in excess, the use of a Gooch-Munroe-Neubauer crucible seemed to be attended with danger on account of solution of platinum. Such a possibility has already been pointed out (Morse, "Exercises in Quantitative Chemistry," 1905, p. 203), and an actual loss was found to take place in blank experiments carried out at the beginning of this research. Accordingly, the ordinary platinum Gooch crucible with an asbestos mat was used.

The precipitated silver chloride or silver bromide was next collected upon the weighed Gooch crucible, dried, and weighed. The moisture retained by the precipitate was determined by fusion in a porcelain crucible, and the asbestos mechanically detached from the Gooch crucible was collected upon a small filter. (For details concerning these operations see Richards and Wells, *Journ. Am. Chem. Soc.*, 1905, xxvii., 515; Baxter, *Journ. Am. Chem. Soc.*, 1906, xxviii., 1329).

Another correction was necessary. The filtrate contained dissolved silver salt, even though an excess of halogen acid was used in the precipitation. The larger part of the dissolved halide is due to the marked solubility in solutions of chromic salts, the amount dissolved increasing with increasing concentration of the chromic salts. Berlin overlooked the correction, which was afterwards pointed out by Siewert. Meineke later determined experimentally the quantity of dissolved material, and also proposed the method of separation which was adopted in this work. The entire filtrate of 3 to 4 litres was evaporated to small bulk, nearly neutralised with ammonia, and then the silver was precipitated from hot solution as a sulphide. The precipitate was collected upon a filter-paper, which was ignited. The residue was converted to the nitrate by digestion with dilute nitric acid, and the solution was then filtered into a graduated flask, in which it was diluted to known volume. By comparison in the nephelometer of this solution with standard solutions of silver, the quantity of silver in solution was determined. In using the nephelometer all necessary precautions, as pointed out by Richards, were taken (*Am. Chem. Journ.*, 1906, xxxv., 510).

That all the dissolved silver was recovered in this way was shown by adding an excess of ammonia to the filtrate of the silver sulphide in one analysis, the hydrogen sulphide having been expelled, and after removal of the chromic hydroxide by filtration, testing the acidified filtrate for silver. None could be detected.

The Determination of Moisture in Silver Chromate.—The proportion of moisture in the silver chromate was found by fusing weighed quantities of the salt in a current of pure dry air, and collecting the water vapour produced

in a weighed phosphorus pentoxide tube. During the fusion of the salt, oxygen is evolved, but since the fusing-point is low, there is no danger of volatilisation of either silver or chromium compounds.

In order to avoid the necessity of removing the fused silver chromate from a platinum boat, boats of copper foil which had been cleaned and ignited were employed.

It was desirable to determine not only whether the proportion of water could be made constant at any one temperature, but also how much the proportion of water is affected by variations in temperature. Experiments were therefore carried out with silver chromate which had been dried for two hours at 200°, 225°, and 300°, in dry air which had been purified as previously described.

After the salt had been dried, a carefully weighed U-tube containing re-sublimed phosphorus pentoxide was attached to the end of the tube. This U-tube was provided with ground glass stopcocks lubricated with Ramsay desiccator grease. The silver chromate was gradually heated until fusion took place, and a slow current of air was allowed to pass through the system for one-half hour in order to make certain that all moisture was carried into the absorption tube. Finally, the phosphorus pentoxide tube was re-weighed.

Temperature of heating.	Weight of silver chromate. Grms.	Weight of water. Grm.	Per cent of water.
200°	4.87	0.00097	0.0199
200°	4.74	0.00098	0.0207
200°	4.43	0.00093	0.0210
Average			0.0205
225°	9.01	0.00136	0.0151
225°	10.85	0.00188	0.0173
225°	10.11	0.00125	0.0124
225°	7.95	0.00105	0.0132
225°	8.23	0.00114	0.0139
Average			0.0144
300°	3.50	0.00034	0.0097

The pentoxide tube was weighed by substitution with the use of a counterpoise of the same size and weight. Before being weighed, both tubes were carefully wiped with a damp cloth, and were allowed to stand near the balance case for thirty minutes. Care was taken to equalise the pressure inside and outside the tubes by opening one stopcock immediately before hanging on the balance.

In order to test the efficiency of the drying apparatus, blank experiments were carried out by allowing a slow current of air to pass through the apparatus into the weighed pentoxide tube. The variations in the weight of the tube were never much larger than the probable error in weighing the tubes.

As is to be expected, the water content gradually decreases with increasing temperature of heating. The extreme variations with specimens of silver chromate which have been heated at 225° amount to only five-thousandths of a per cent. Evidently the percentage of residual water is as constant as can be reasonably expected, and the mean can safely be assumed to represent with sufficient exactness the average proportion of water in the salt. Hence, from every apparent grm. of silver chromate, 0.000144 grm. is subtracted.

(To be continued)

Decomposition of Carbon Dioxide by Ultra-violet Rays.—H. Hercheffinkel.—Carbon dioxide is decomposed into carbon monoxide and oxygen by the ultra-violet light of a quartz mercury lamp. Radium emanation, when it acts on carbon dioxide, also produces a measurable amount of carbon monoxide.—*Comptes Rendus*, cxlix., No. 6.

THE ESTIMATION OF CARBON MONOXIDE IN MINE GAS.*

By E. H. WEISKOPF, Ph.D., F.C.S.

MR. CULLEN, in his paper on "The Gases Resulting from the Use of High Explosives" (*Journ. Chem. Met. and Mining Soc. of South Africa*, November, 1908, p. 144), foreshadowed the reading of another, dealing with the methods by which the analytical results involved were obtained.

The work carried out may conveniently be considered under three distinct headings, viz. :—

Firstly.—The gas-volumetric determination of the products of explosion and of mine air.

Secondly.—The estimation of carbon monoxide.

Thirdly.—The calculation of the results obtained and their practical application.

From the title of my paper you will observe that I intend to deal with the estimation of carbon monoxide only, and am thus only partly redeeming the pledge given by Mr. Cullen. I consider it advisable therefore to explain my reasons for deviating from the original plan. With regard to the first sub-division of the subject, the principles and methods of the exact volumetric analysis of the gases involved have been so exhaustively dealt with in the various standard works, that I am sure you will not suspect me of having been foolish enough to strike out on my own and try to improve on the methods of such master-minds as Bunsen, Winkler, or Hempel. A recapitulation of their methods, therefore, would serve no useful purpose. Although I have not followed the classical methods of Bunsen, who for exact analysis avoids even the employment of liquid absorbers, I may conscientiously say that every *finesse* and improvement which literature and experience suggests has been taken advantage of. If I say that the gases were displaced from the original sample bottles by means of mercury; that they were kept throughout the analysis in a water-saturated state; that they were collected and measured over mercury in a carefully calibrated measuring tube of 140 cc. capacity; that this tube was placed inside a water-jacket, whose temperature was read to within 1/10 C.; that the levelling and reading of the mercury in the measurer was accomplished by means of a cathometer to within 0.05 cc., and that the barometric pressure, corrected for temperature and expansion of scale, was read to within 0.05 mm., I feel sure that you will share my conviction that a high degree of accuracy in the results obtained has been achieved. Beyond this, and apart from the fact that our results are more accurate than those obtained by previous workers on these fields, they have brought out no new or noteworthy facts, excepting perhaps our inability to find olefines in the mine gases. In consideration of all the foregoing I trust you will agree that a more detailed elaboration of the gas-volumetric methods employed would be mere waste of time.

With reference to the third sub-division of the paper, i.e., the calculation of the results obtained and their application to practice, I do not propose to weary you with the details of the stoichiometric calculations, but I may state that in the appendix to this paper will be found a complete record of actual figures and data involved in the course of the analysis of a mine gas before and after blasting.

Particular attention is invited to the method of determining the quantity of gas taken for analysis in the gravimetric estimations of carbon dioxide and monoxide, which is a departure from the usual. As doubts have been expressed as to its accuracy, I have thought it advisable to elaborate it fully in the appendix. As to the stating of the analytical results in a manner suitable for applying

* From the *Journal of the Chemical, Metallurgical, and Mining Society of South Africa*, February, 1909.

them to practice, there is to my mind only one way, namely, the statement of gases actually evolved in the drill-hole. The mere record of having found, say, 1.2 per cent CO in the sample may be a correct expression of the analytical results, but it conveys nothing to us, because there is no apparent connection with any of the essential points at issue. These, to my mind, from the practical, the physical, and the chemical points of view are:—

To what extent does the use of a known kind and amount of explosive vitiate the mine air?

To what extent are the results affected by the usual methods of charging, tamping, and firing? and

To what extent are the results affected by the nature and composition of the explosive used?

The first of these points, involving, as it does, the health conditions underground, is, of course, of paramount interest. The natural remedy is efficient ventilation, and the whole subject might perhaps be left at that. To the scientist, however, the two other points are just as important and probably more interesting, and this for the reason that a proper understanding of their causation may lead us to do even better than cope with the noxious gases once liberated, namely, to prevent their formation. There is yet another aspect of the question which offers a good deal of temptation to many of us, and that is, the great scope it affords for the evolution of fantastic theories. On this subject I shall have to offer a few remarks later on, but meantime I shall proceed with the main purpose of my paper, which is to prove that carbon monoxide is formed in considerable quantities in blasting operations underground. The importance of this really requires no elaboration, but it may be as well to recall the fact that Mr. Mann, who carried out a very elaborate investigation in Western Australia on behalf of a Royal Commission on the "Ventilation and Sanitation of Mines," came to the conclusion that under normal conditions carbon monoxide is not formed, or only in inappreciable quantities. On the other hand, to Dr. Moir and Mr. Heymann, in their investigations carried out for the Miners' Phthisis Commission, belongs the credit of having been the first, in this country at any rate, to prove the presence of carbon monoxide in mine gases; and if their labours have been less appreciated and more sceptically received than they deserve, the inconsistency of the results in some cases probably accounts for it. Generally speaking, there are at the present moment very many people who are inclined to doubt the fact that considerable amounts of carbon monoxide are formed underground, and to convince them that there is no possibility of error, and that the methods and apparatus employed by us for its estimation are in principle and application correct, shall be my endeavour to-night.

Sampling, no matter for what purpose, is a most important step in any investigation, and in this case particular pains were taken to eliminate all sources of error. Although we desired to interfere as little as possible with the ordinary underground conditions, we considered it of advantage to obtain the gases given off by the explosion in as concentrated a state as possible, not only to increase the accuracy of the final results, but also to minimise the risk of overlooking some of the possible products, which might be present in small fractions of 1 per cent only. The high percentage of CO₂ found in the samples is sufficient evidence that this was achieved. The actual method of sampling employed has been described by Mr. Cullen in his recent paper (see *Journ. Chem. Met. and Mining Soc. of South Africa*, 1908, p. 144), and it is therefore unnecessary to add anything further. It might, however, be of interest to note, that although the sample bottles throughout were provided with glass taps, there was, contrary to text-book opinion, no trouble with them. This is probably due to the very superior make which manufacturers are able to supply nowadays, and also to the precaution of tying down the keys with rubber bands, thus ensuring against accidental loosening or moving.

After many experiments with various methods for estimating carbon monoxide, the iodine pentoxide method was finally decided upon. This method is based on the fact first observed by Ditte in 1870 (*Bull. Soc. Chim.*, 1870, xiii., 318), that the iodic acid or its anhydride oxidises carbon monoxide to carbonic acid, liberating at the same time an equivalent amount of iodine.

La Harpe and Reverdin described a method for detecting CO in air as early as 1889 by passing it over iodic acid contained in a flask, which was heated to 150° C. (*Bull. Soc. Chim.*, 1889, li., p. 163). The vessel was provided with a bent side-tube which dipped into starch solution. The authors found that one to two parts of CO per thousand showed appreciable coloration due to liberated iodine.

That the reaction involved, $5\text{CO} + \text{I}_2\text{O}_5 = \text{I}_2 + 5\text{CO}_2$, is very sensitive and applicable for the quantitative estimation of traces of CO in gases, was first of all demonstrated by Maurice Nicloux in April, 1898 (*Comptes Rendus*, 1898, cxxvi., 746). He employed iodic acid at a temperature of 150° C. for the oxidation of the carbon monoxide, and realised the importance of removing carbon dioxide, sulphur dioxide, and sulphuretted hydrogen from the gases before passing through the iodic-acid tube. He estimated the amount of iodine liberated by comparison with solutions containing known amounts of iodine in carbon disulphide.

Armand Gautier (*Comptes Rendus*, 1898, cxxvi., 793) referring to this publication, stated that he had employed this method for the past seven or eight years in his laboratory. In another communication, dealing with the determination of traces of carbon monoxide in air, he states (*Comptes Rendus*, 1898, cxxvi., 871) that he had tried CO estimations in gas-mixtures of a dilution corresponding to that in the atmosphere of towns, by absorption with cuprous chloride or ammoniacal silver nitrate solution, and also by oxidation with permanganate and other reagents. None of these methods, however, gave satisfactory results. He was then experimenting with iodine pentoxide at a temperature of 60° C. Some of the experiments he published a month later (*Comptes Rendus*, 1898, cxxvi., 931). He found that CO begins to react on I₂O₅ at 30° C. The action becomes more pronounced at 40° to 45° C., and is complete at 60° to 65° C. It takes place, no matter what the dilution may be. He investigated several means of determining the amount of iodine liberated, by directly weighing it in absorption tubes filled with silver or copper filings and also by certain volumetric methods. Neither of these methods proved sufficiently accurate, and the author had recourse to Müntz and Aubin's method (*Ann. d'Inst. Agron.*, 1881-1882), which consists in collecting the carbon dioxide formed in KOH solution, subsequently liberating it again with sulphuric acid, and measuring over mercury. Test analyses given in detail show the accuracy of the method. Later in the same year (*Comptes Rendus*, 1898, cxxvi., 1299) Gautier published a long paper on the estimation of CO in the atmosphere of Paris. In the course of it he states that in continuation of the above mentioned research work, he had been successful in evolving a very accurate method, capable of determining amounts of CO in the air as small as 1 in 500,000. I may here mention that in order to achieve these results he had to use samples as large as 200 litres. This method differed from that employed by Nicloux only inasmuch as the iodine liberated from the iodine pentoxide was caught in another tube over metallic copper, the amount being ascertained by direct weighing. The author particularly refers to the fact that the presence of certain hydrocarbons, notably ethylene and acetylene, influences the accuracy of the results. He now considered 100° to 105° C. the most suitable temperature for the reaction. It is, however, noteworthy that, in order to prepare the iodine pentoxide tube for weighing, he subjected it to a current of dry air at a temperature of 220° C. This is entirely in accord with the results obtained during our investigations, viz., that at temperatures up to 200° C. the iodine pentoxide, provided,

of course, that it has been prepared with reasonable care, is absolutely stable.

To those who are incredulous about the presence of CO in the atmosphere surrounding industrial centres, it may be interesting to note that Gautier found amounts of CO in the atmosphere of Paris varying between 0 and 9 parts per million. He also analysed samples of laboratory air containing considerably more.

There seems to have been a long period of inactivity after the foregoing publications, the next record of note being that of Kinnecutt and Sanford in 1900 (*Journ. Am. Chem. Soc.*, 1900, xxii., 14). These authors could not obtain good results by either of the methods of Gautier and Nicloux on account of the impossibility of accurately determining the amount of iodine liberated by directly weighing it, or estimating it colorimetrically. They also stated that the gravimetric method of determining the carbon dioxide liberated during the reaction was unsatisfactory. They asserted, however, that if the iodine be caught in potassium iodide solution and subsequently titrated with thiosulphate of sodium, very close and accurate results could be obtained. Their results are in close agreement with theoretical mixtures subjected to analysis, and showed that the method is capable of determining as little as 0.0025 per cent of carbon monoxide in the air. The authors further stated that they had proved experimentally

lengthy paper by himself and Clausmann (*Comptes Rendus*, 1906, cxlii., 485), and as a result of very carefully conducted and extensive experiments, they came to conclusions which have a very important bearing on our subject, because they not only confirm the accuracy of the I_2O_5 method, but also give specific reasons for the unreliability of gas volumetric determinations of CO in gaseous mixtures. Their conclusions may be summarised as follows:—

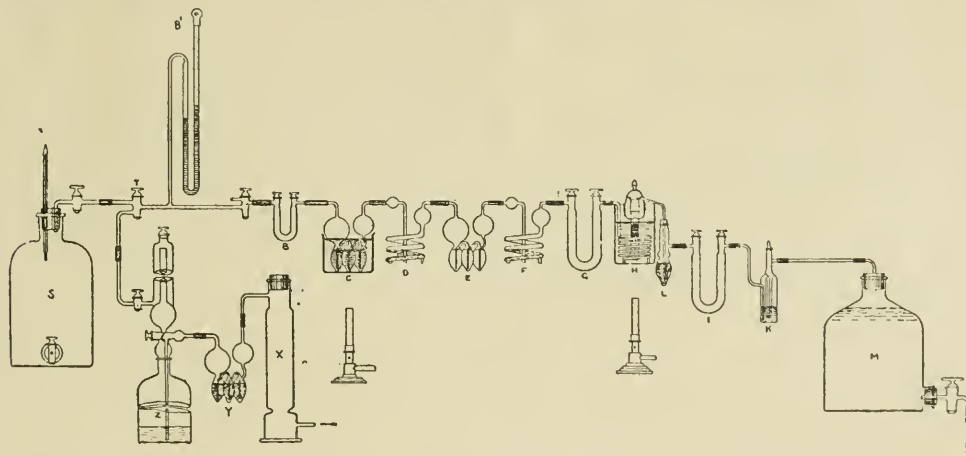
Firstly.—In determining CO when present in mixtures to the extent of several cubic centimetres, and after the gas in the ordinary course of analysis had been washed with KOH, bromine water, and pyrogallol, the cuprous chloride solution, even when used in considerable excess, does not absorb all the carbon monoxide.

Secondly.—CO diluted with an inert gas does not burn completely even when exploded in the presence of an excess of oxygen.

Thirdly.—The remainder of the CO escaping estimation by either of the above methods can only be determined correctly by passing it through iodine pentoxide at temperatures of not less than 70° C.

These precise statements should make it clear why the absorption method employed by some has seemingly given negative results.

With reference to the combustion method we have never attempted the explosion with excess of oxygen, but have



that other constituents of coal-gas do not influence the accuracy of the method.

In 1903 Fillunger mentioned (*Chem. Ztg.*, 1903, 27) that Moltersky and Nowicky employed a method similar to that just referred to, but they neglected the iodine liberated and only determined the CO_2 produced by absorption in $Ba(OH)_2$ solution and subsequent titration. The authors further asserted that hydrocarbons in the mixture had no effect upon the results. They claim an accuracy of 0.01 to 0.1 per cent of the theoretical.

In 1905, Lévy and Pécoult (*Comptes Rendus*, 1905, cxl., 98) reverted back to Nicloux's method for the estimation of CO in confined atmospheres, but employed chloroform instead of carbon disulphide for the colorimetric estimation. In a further communication a year later (*Comptes Rendus*, 1906, cxlii., 162), the same authors confirmed their previous results, and asserted that small amounts of acetylene did not seriously interfere with the accuracy of the method. They found that, while four parts of acetylene per thousand produce a very slight coloration, one part of CO per 10,000 produced an intense colour due to iodine liberated. They therefore came to the conclusion that, in testing normal air for CO, the possible presence of acetylene may be neglected.

In the meantime Gautier seems to have busied himself with the problem of why the volumetric estimation of CO with cuprous chloride gave such unreliable results. In a

obtained excellent results with combustion over spongy palladium. In a synthetic gas mixture employed by us containing—

1.018 vol. per cent CO	
0.867 "	H
0.767 "	C_2H_4
4.010 "	CO_2
1.047 "	CH_4
19.210 "	O
73.081 "	N

we found, after elimination of the ethylene and CO_2 :—1.02 vol. per cent CO and 0.85 vol. per cent H by passing the mixture through spongy palladium at a temperature of about 300° C. It will be noted from the foregoing results that the combustion is quantitative, and also that the methane present remains unaffected.

Of the more recent publications on the estimation of carbon monoxide I can find only two worthy of notice. One by J. Tôth (*Chem. Ztg.*, 1907, ix., 98), who employed the method elaborated by Kinnecutt and Sanford, for the estimation of CO in the smoke of tobacco. He filters the dried gases through cotton-wool, and before passing them through the pentoxide tube contained in a glycerin bath of 60° to 70° C., he purifies them in succession with 10 per cent caustic potash, baryta water, sulphuric acid, and quicklime.

The other publication by Morgan and McWorther (*Journ. Am. Chem. Soc.*, 1907, xxix., 1589) deals exhaustively with the subject. They confirm that with Kinnecutt and Sanford's method good results can be obtained. Subsequently, however, they used a modification of the method, which consists in passing the gas, after it has left the iodine pentoxide tube and been freed from all iodine fumes, through a long test-tube containing barium-hydroxide solution of known strength, titrating the excess of alkali with oxalic acid, using phenolphthalein as indicator. They have proved experimentally that this method agrees well with the titration of the iodine caught in potassium iodide. They make much of the fact that lubricants used for the glass stoppers of the iodine pentoxide tube have a tendency to creep inside, thus upsetting the accuracy of the results; as, furthermore, the employment of rubber or cork stoppers is, of course, out of the question, they express their surprise that none of the other investigators of the subject have found it worth while to draw attention to this matter. The authors, in order to get over this difficulty, have employed and recommend the radical measure of doing away with glass stoppers altogether, by using sealed glass connections only, and there is no doubt this does away with all chances of the lubricant interfering with the reaction.

As these measures have not been strictly followed in our experiments, it might not be out of place to mention our reasons for departing from them. In the first instance, a tube with the iodine pentoxide enclosed was not available, and we also foresaw some difficulty in removing the sublimed iodine quantitatively from the inner walls of the delivery tube. On the other hand, a spiral tube, such as Prof. Will had first of all employed for decomposing nitro-cotton (*Zeit. Angew. Chemie*, 1901, 743), offered very great advantages both as regards handling and working. We found that, provided the hood is clamped to the body by means of springs (see H in illustration) the joint holds absolutely tight without the use of any lubricant. The large and well ground surfaces in connection with the above arrangement being so close fitting, also effectually prevent the tendency of the oil from the heating bath to creep up. This has been proved not only by the consistency of our results and the close agreement of analysis of synthetical gas mixtures, but also by repeated "blanks," extending over periods of several hours.

From all the foregoing it is clear that, although a great amount of research work had been carried out, there is a good deal of contradiction between the opinions of various workers, particularly with reference to the effect of certain gases, and also to the final determination of the products of the reaction. As regards the main principle of the method there is, however, only one opinion, viz., that the reaction involved by the passing of the CO over iodine pentoxide at temperatures from 70° to 150° C. is admirably suitable for its quantitative determination, and cannot be surpassed as regards delicacy and accuracy of the results obtained. Our decision, therefore, in selecting this method for the estimation of CO in mine gases should not require further justification.

The modifications introduced and the arrangement of the apparatus finally employed by us are the outcome of numerous experiments and extensive research, covering practically all the ground traversed by previous investigators. These experiments are too lengthy and complicated to be elaborated upon in these pages. Suffice it to say that by check-analyses, blanks, employment of synthetical gas mixtures, and all other means at our disposal, we have verified the accuracy of the results obtained. As an example, I will only mention that in a gas mixture containing 0.999 vol. per cent CO and 4.00 vol. per cent CO₂ and approximately known quantities of methane, ethylene, hydrogen, nitric monoxide, oxygen, and nitrogen, we found 0.97 vol. per cent CO and 4.11 vol. per cent CO₂.

One other point might be specially mentioned, and that is the fact that ordinary sulphuric acid, even when as many as three absorption coils are used, does not prevent

olefines passing to the iodine pentoxide tube, where, of course, they are oxidised, liberating correspondingly large amounts of iodine. We have proved this to be the case with synthetical gas mixtures containing as little as 0.251 per cent ethylene. In the course of our investigations it has been found that, although by increasing the number of sulphuric tubes and by keeping them at a temperature of 160° to 170° C., the amounts of ethylene passing on were decreased; complete retention was only achieved by employing sulphuric acid of a strength of 99 to 99.5 per cent H₂SO₄ and keeping the bulbs containing it at a temperature of 165° C.

In now describing the actual apparatus, it will be observed that provision has been made to keep the pressure within it at figures very little above the normal. This state of affairs ensures against undue strain being put on the various connections and joints, and is effected by the aspirator, M, taking off part of the resistance which the gases displaced from the sample bottle have to encounter. The two-way tap, T, in front of the mercury gauge, B¹, which latter, by means of a vernier and mirror reflector, can be read to within 0.1 mill., allows of filling the apparatus with dried and purified air. The air used for this purpose has passed the chloride of calcium tower, X, the Liebig bulbs, Y, containing palladium chloride, and the washing and drying apparatus, Z, which contains caustic potash solution and soda-lime. At the end of the operation, when the required amount of gas sample has been taken, the whole apparatus is again flushed out with pure air until all of the sample has been displaced.

The gases in their course to the iodine tube, H, pass first of all a U-tube, B, filled with glass-wool and pumice saturated with sulphuric acid, in order to keep back organic and inorganic dust and moisture. They next pass through Liebig bulbs, C, filled with 99 per cent sulphuric acid, kept at a temperature of 165° C., and then through the sulphuric acid spiral, D. The gases now go through the carbonic acid absorption apparatus, which consists of the caustic potash bulb, E, the sulphuric acid spiral, F, and a U-tube, G, filled with pumice moistened with sulphuric acid. This arrangement was found necessary, as accurate results with the usual bulbs with calcium chloride tube attached were not obtained. The iodine pentoxide spiral tube, H, through which the gas next passes, is contained in an oil-bath at a temperature of 150° C. As will be seen the delivery tube dips directly into the absorption tube, L, containing 5 cc. of a 15 per cent potassium iodide solution. The gases finally are dried in the U-tube, I, and the CO₂ formed by the reaction is caught in the small apparatus, K.

If H₂S be suspected in the sample an absorption tube containing acidulated lead acetate solution, or a tube containing pumice saturated with copper sulphate and dried at 150° C., must be inserted in front of the first sulphuric bulb.

In cases where methane is present, we have estimated it in a porcelain tube containing copper oxide by the ordinary combustion method. This tube in such instances was inserted between the aspirator bottle and the end of the apparatus just described. With this I bring my remarks on the methods employed by us to a conclusion.

(To be continued).

THE FERMENTATION INDUSTRIES.

THE inaugural lecture of the courses of instruction on the Fermentation Industries, held at the Sir John Cass Technical Institute, Aldgate, was given on Tuesday, October 5th by Mr. A. R. Ling, the lecturer on Brewing.

Dr. A. L. STERN, of Messrs. Bass, Ratcliff, and Gtrettton, presided, and in urging the importance of scientific investigation he met the criticism that such work should not be wasted on such a commonplace subject as brewing by the reminder that Pasteur's great work on bacteriology which in itself has done so much to alleviate human suffering, and was the pioneer work of an immense amount of in-

vestigation which has resulted in incalculable benefit to humanity, was initiated by the study of the troubles of the vintner and brewer.

Mr. ARTHUR LING, whose subject was "Chemistry in Relation to Brewing and Malting," said the object of the lectures was to enable brewers and maltsters to gain an insight into the principles underlying their daily operations in the light of modern scientific knowledge. After dwelling on the importance of chemistry to industries generally, he pointed out that the researches in physiological chemistry, which had been conducted with the object of gaining an understanding of the principles of brewing and malting by such men as the late Cornelius O'Sullivan (the chairman's predecessor) and by Dr. Horace T. Brown, had been of the highest moment for science generally. In Liebig's time fermentation was regarded as a purely chemical phenomenon, and the biological aspect of the subject owed its origin to the discoveries of Pasteur. In recent years, however, the chemistry of fermentation had been resuscitated by Buchner's discovery of the cell-free fermentation, which had been confirmed and extended by the work of Dr. Harden, their lecturer in micro-biology. Important though the application of biology was to the fermentation industries, Mr. Ling urged that it was quite useless if dissociated from chemistry. The chief factor in deciding whether or not a given organism would develop was the constitution of the soil in which it was sown. In the case of brewing materials the constitution of the nitrogenous constituents as well as of the carbohydrates determined whether organisms which produced sound or unsound beer would gain the mastery; and in this connection he referred to the recent researches of Dr. Horace T. Brown on the nitrogen question in brewing, and to the discoveries of Dr. F. Ehrlich, of Berlin, on the origin of the secondary products of fermentation. Mr. Ling then gave an account of his own researches on the production of diastase during the germination of barley on the malting floors. The results confirmed those of Brown and Morris, that the major portion of the diastase is located near the epithelial layer, and showed the importance in practice of slow cool germination and of efficient withering.

The proceedings concluded with a cordial vote of thanks to Dr. Stern, proposed by Mr. GEORGE BAKER, Chairman of the Institute Committee, and seconded by Dr. ARTHUR HARDEN, F.R.S., the lecturer on the Micro-biology of the Fermentation Industries at the Institute.

The new micro-biology laboratory, which has recently been equipped by the Governors of the Institute, was thrown open to visitors at the close of the lecture. This laboratory is well equipped for all subjects of micro-biological work in connection with the fermentation industries, systematic courses of instruction in which commenced on Tuesday, October 12th. Full details of the courses may be had on application at the Institute.

PROCEEDINGS OF SOCIETIES.

MANCHESTER LITERARY AND PHILOSOPHICAL SOCIETY.

THE first meeting of the session was held on Tuesday, October 5th, at its House in George Street. Mr. FRANCIS JONES, M.Sc., F.R.S.E., President, occupied the Chair.

Dr. HENRY WILDE, F.R.S., read a paper entitled "On a New Binary Progression of the Planetary Distances and on the Mutability of the Solar System."

Reference was briefly made by the author to his paper read before the Society in March last, on his demonstration and discovery that the moving force of celestial bodies is as the square of the velocity, and inversely proportional to the square of the distance. Dr. Wilde has adopted in his

table of planetary orbits the radius vector of Mercury as the most natural and convenient unit to which the other planetary distances should be referred, the terrestrial unit being an obvious survival of the geocentric system of the universe. The change in the unit of distance has revealed a new binary progression of the planetary distances, much nearer the observations than that of Bode's law, and removes the principal ground of objection made by some astronomers to rank the binary progression as a law of nature. The author has demonstrated that the anomalous minus distance of Neptune from the progression is caused primarily by its outermost position in the planetary system, with the consequent united attractions of all the planets upon Neptune. The inevitable effect of the outermost position of a planet to contract continuously its radius vector has never presented itself to Lagrange, Laplace, and other writers on celestial mechanics who have elaborated the doctrine of the absolute stability of the solar system. The author has further demonstrated that the final effect of the continuous contraction of an outermost planet would be to cause all the planetary bodies to coalesce in succession to form one or more self-luminous bodies revolving round the sun as binary or ternary revolving stars, of which upwards of ten thousand have been discovered during the last century in the immensity of the stellar universe.

NOTICES OF BOOKS.

An Atlas of Absorption Spectra. By C. E. KENNETH MEES, D.Sc. (Lond.). London, New York, Bombay, and Calcutta: Longmans, Green, and Co. Croydon: Wratten and Wainwright, Ltd. 1909.

THE above atlas is the outcome of an investigation of the absorption of light by a large number of organic compounds, both in aqueous solution and in gelatin films. The work is confined to the visible and infra-red radiation between $\lambda = 3900$ and $\lambda = 8000$, and the records are obtained upon a "Wratten spectrum panchromatic plate" which is almost evenly sensitive between these points. No attempt is made to examine absorption in the ultra-violet, which has already been studied by Messrs. Uhler and Wood, and the results published by the Carnegie Institute of Washington.

The solutions are contained in a wedge-shaped cell fixed in front of a long horizontal slit, so that the thickness of solution varies from end to end in the ratio of about 1 to 15.

The gelatin films are prepared by combining the dye with gelatin solution, coating glass, and stripping when dry, and the graphic representation of the variations in absorption with wave-length is obtained not, as in the case of the solutions, by reducing the thickness of the absorbent, but by superposing upon the film a wedge of neutral tinted black glass.

Photographic records are given of some 170 different dye-stuffs, with particulars of the "stability to light" and the strength of solution used. Records are also given of the absorption of a large number of gelatin filters prepared and stocked by Messrs. Wratten and Wainwright.

Dr. Mees has already done great service to science by his numerous researches upon the action of light upon photographic films, and by the commercial production of a photographic plate uniformly sensitive down to the infra-red, and the above atlas is an unpretentious but none the less valuable record of painstaking investigation.

Elementary Chemistry. By HOLLIS GODFREY. New York, London, Bombay, and Calcutta: Longmans, Green, and Co. 1909.

THIS work represents a new type of school book to be put into the hands of beginners, and there is much in it that

will commend itself both to teacher and student. For one thing, it is more interesting than the general run of similar books, and the connection between scientific knowledge and every-day practice is constantly emphasised. The "chemistry of daily life" is met with in every chapter and much miscellaneous information which is certain to make an impression on the student's mind is included. The illustrations are of the type now commonly adopted in new geographical books, and although their bearing on the text is not always very apparent, the interest of the reader may sometimes be stimulated by them. A full year's course of theoretical and descriptive work is contained in the book, the text of which is to a certain extent marred by a somewhat florid and sensational style of writing. In an appendix each chapter is epitomised so that the chief facts in it may be rapidly revised, and also a set of questions is given on the subjects of every chapter; these appear more than ordinarily futile, for no attempt is made in them to exercise the student's power of thought and reasoning. The only possible use for them is to help the student to grasp the gist of each paragraph more readily, but this is really unnecessary, for the style is easy enough to present no difficulties even to the youngest beginner.

Adits to the Analysis of Food and Drugs. By C. G. MOOR, M.A. (Cantab.), F.I.C., and WILLIAM PARTRIDGE, F.I.C. Third Edition. London: Baillière, Tindall, and Cox. 1909.

IN this book, the third edition of which has been thoroughly revised and almost re-written, short descriptions are given of the usual methods of analysing and detecting the presence of adulterants and impurities in common articles of food, and some notes are added on the British Pharmacopœia and methods of testing a few drugs. Microscopical tests are either neglected altogether or else are very shortly treated, and a serious defect with regard to them is the absence of illustrations; it is practically impossible to give a satisfactory verbal description of the different forms of starch, for instance. It is, moreover, not difficult to find places in which the authors have dismissed processes of importance rather summarily; for example, Hinks' qualitative test for the detection of cocoa-nut oil in butter, which is merely mentioned, is a very useful method, well worth detailed notice, and Hanus' test for the same purpose also seems reliable. The colouring matters used for milk are very shortly treated, but at the same time the book does not aspire to completeness, and as a supplementary aid the third edition will serve the same useful purpose as its predecessors.

Analyse des Metaux par Electrolyse. ("The Analysis of Metals by Electrolysis"). By A. HOLLARD and L. BERTIAUX. Paris: H. Dunod et E. Pinat. 1909.

THE theory and principles of the separation of metals by electrolysis are very simply stated in this book, in which an attempt is made to present a rational classification of the metals to serve as a basis for their separation by electrochemical methods. General methods of separation are discussed in the first part, and then the most important metals are treated individually, full experimental details of the processes employed being included. Applications to industrial products form the subject of the third part of the book, and very useful tables of experimental results are given. Although important and valuable additions have been made to the second edition the treatment of the subject still remains very slight in comparison with that to be found in the standard laboratory text-books of electrolytic analysis. However, the details of many methods of separation are arranged in the book in convenient form, and the authors vouch for the reliability of all the processes described.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlix., No. 5, August 2, 1909.

Latent Heat of Fusion and Specific Heat of Propionic Acid.—G. Massol and M. A. Faucon.—The latent heat of fusion of propionic acid is found by experiment to be 23.35 cal. (for 1 grm.), whereas the general relations of Raoult, van't Hoff, and Forcrand would give rather higher values. The specific heat in the solid state, taken between -46° and -19.8° , is equal to 0.728; i.e., it is higher than the specific heat in the liquid state. These different results can be explained by the fact that for substances which have recently been solidified the liberation of the latent heat is not complete.

Ethylenic Derivatives containing Nitrogen.—G. Busignies.—When the organo-magnesium derivatives of alkyl halogens, in which the halogen group is united with CH_2 or CH , reacts with amido- or alkyl-amido ketones, basic ethylenic amines are obtained. Thus the two compounds $\text{CH}_2 = \text{C} = [\text{C}_6\text{H}_4 - \text{N} - (\text{CH}_3)_2]_2$ and $\text{CH}_3 - \text{CH} = \text{C} = [\text{C}_6\text{H}_4 - \text{N} - (\text{CH}_3)_2]_2$, fusing at 115° and 99° respectively, can be obtained by this method. The author has prepared many similar products, and has found that both they and the saturated compounds derived from them by the fixation of two atoms of hydrogen have very marked basic properties. They are insoluble in water, soluble in organic solvents and in dilute acids, giving salts and double salts.

MISCELLANEOUS.

Action of Gravity on Induced Activity of Radium.—Louis Wertenstein.—The author has studied the difference in the active deposits on the two faces of two horizontal plates facing one another, as a function of the time which has elapsed since the action of the emanation ceased. He found that the induced activity which is deposited by the action of gravity contains no radium A, and this experimental fact can be explained by supposing that the fall of the deposit takes enough time to allow of the disappearance of the radium A. Using Debiere's apparatus for the study of the change brought about by the action of gravity in the shape of the curves which represent the value of the activity of the discs as a function of their distance, the author found that the surfaces turned downwards had a maximum of activity for distances between 1 cm. and 1.5 cm., and the activity diminished as the distance increased. The upper surfaces had activities proportional to their distances for small distances, and equal to those of the corresponding faces turned downwards; as the distances increased the shapes of the curves depended upon the moisture of the air and fell into three different classes. When the distance between the plates was such that a particle in falling from one surface to the other would lose all its activity during its fall, the activity of the face turned upwards ceased to increase with the distance. By using Stokes's Law to calculate the diameter of the particles it may be shown that in certain cases they may attain ultra-microscopic dimensions.—*Comptes Rendus*, cxlix., No. 4.

MEETINGS FOR THE WEEK.

WEDNESDAY, 20th.—Microscopical, 8. "Microscopical Structure of an Inoceramus Limestone in the Queensland Cretaceous Rocks," by F. Chapman. Exhibition of Slides of Foraminifera from the Collection of the late Wm. Kitchen Parker.

FRIDAY, 22nd.—Physical, 5. "Cadmium Amalgams and the Normal Weston Cell," by F. E. Smith. "Production of Helium from Uranium and Thorium" and "Production of Radium from Uranium," by F. Soddy. "A Gravitational Problem," by C. V. Burton.

THE CHEMICAL NEWS.

Vol. C., No. 2604.

THE UTILISATION OF SPENT HOPS.

By CLAYTON BEADLE and HENRY P. STEVENS.

THE above product is practically useless, and at present is utilised chiefly by digging it in with farm-yard manure. Attempts have from time to time been made to convert it into paper, but for such purposes it is worth next to nothing; in fact, it is not worth the carting from a brewery to a paper-mill; moreover, it could only be of service in the very cheapest rough packing paper or boards.

The only feasible utilisation appears to be in the direction of a food-stuff for cattle; in its usual form, however, it is quite useless in this direction. The chief disqualification for this purpose is the hard resistant woody fibre that it contains.

Recent work of ours on the hydrolysis of cellulose, whereby the same has been transformed from a useless indigestible to a nutritious digestible product, has, in our opinion, rendered it possible to utilise materials such as spent hops to advantage.

We have shown ("By-products of Cotton Seed and their Utilisation," *Journ. Soc. Chem. Ind.*, Oct. 15, 1909, p. 1015) that products, such as cotton-seed hulls, when hydrolysed according to our process (British Patent 12,718, 1906), are converted into a fine grain, smooth meal which can be fed to cattle and sheep with advantage, and that the cellulose, by conversion into hydrocellulose, instead of ranking as "woody fibre" should be classed as "carbohydrates" when calculating for food units.

The above process is usually conducted in charges of half a ton at a time, by raising to a critical temperature in presence of fumes of hydrochloric acid, the whole mass being kept in agitation in a closed vessel. At the critical temperature, something over 100° C., and varying with different materials, the conversion of the cellulose is almost instantaneous. At a somewhat higher temperature, at 120° C., the acid fumes are driven off from the mass, so that it is theoretically possible to effect the conversion without any consumption of acid. In practice, however, the basic constituents of most products of this nature are sufficient to consume from 1 to 2 per cent HCl on weight of product treated. The acid, however, as far as the actual conversion is concerned, does not enter into combination and acts catalytically.

The product after undergoing the hydrolysis is usually allowed to cool, when all further action appears to be arrested, but if heaped up it remains hot for considerable periods, and spontaneously undergoes further changes, whereby the cellulose is more completely "converted," and in the case of cotton-seed hulls, a product (which has been prepared under this process in some thousands of tons) is produced which develops a sweet coffee-like smell and taste and a brown colour. The crispness of its particles renders it possible to easily grind it to the form of a fine meal. The bulk which it occupies in the ground condition is about one-third of that occupied by the untreated material.

As the spent hops after draining contain about 70 per cent of material, and as their physical condition is entirely different from that of such materials as cotton-seed hulls, the problem of conversion is different. The moisture requires to be removed before the conversion can take place. This moisture can, in part, be removed by hydraulic pressure or passing the product through rollers; the remainder can then be removed by heat, but it is best to leave some moisture in before the addition of acid, as the whole mass is more easily permeable in a semi-moist condition.

In some spent hops we have examined, we find in the draining liquor as much as 8 to 10 per cent of sugars on the weight of the dried hops, which by drying down would form part of the food-stuffs.

To give some idea of the constituents after hydrolysis, we give the following figures:—

Hydrolysed Meal made from Spent Hops.

	Sample A. Per cent.	Sample B. Per cent.
Moisture	9.16	10.51
Ash	6.08	6.89
Hydrocellulose .. .	33.62	26.52
Fat	6.39	10.71
Protein	19.35	21.30
Carbohydrates .. .	25.40	24.07
Food units (approx.) ..	89.8	104.1

Albumenoids in aqueous extract of meal = 2.05 per cent.

Samples A and B are from the same brewers and from bulk, and show what might be expected as to composition from different kinds of hops.

The astringent principle of waste hop meal can be counterbalanced by mixing with food-stuffs containing oil, &c. So far no ill-effects have been noticed from use of these spent hops residues, and there is every reason to assume that their food value is equal to the results as indicated by analysis, and that at 1s. per unit the product in its dry condition would be worth about £5 per ton, but that it would have to be used in practice by judicious blending with other materials.

THE ESTIMATION OF CARBON MONOXIDE IN MINE GAS.*

By E. H. WEISKOPF, Ph.D., F.C.S.

(Concluded from p. 194).

THERE still remains the problem of the origin of the carbon monoxide formed. This to my mind, at the present moment, can only be the subject of speculation. My reasons for saying so are, that after all we have not established very much more than the bare fact that carbon monoxide is formed in the drill-hole. It is true that the methods of tamping and blasting generally may reasonably be excluded, not only on account of the particular care exercised during the experiments, but more so by reason of the consistent closeness of the results obtained. These would have been very much more varied if incomplete detonation or partial misfires were entirely responsible for the formation of the incomplete combustion products. This reason has tempted many to assume that the above objectionable gases originate from the explosive. Many theories based on this contention have been brought forward. It has been suggested that the nitro-cotton in the blasting gelatin does not take part in the chemical reaction involved. Others, in expecting nitric oxide as part product of an incomplete detonation, have argued that their inability to find large amounts of this gas is proof conclusive that carbon monoxide is not present either.

Counter arguments have been advanced, that nitrogen peroxide, condensing as nitric and nitrous acid, will to a very great extent escape being caught in the gas sample. Others, again, have been puzzled by the deficiency in oxygen which did not agree with theoretical expectations. A further suggestion has I find been made a considerable time ago by Dr. Moir, that the cartridge-paper introduced with the explosive is responsible for the formation of the products of incomplete combustion (*Proc. Chem. Met. and Mining Soc. of South Africa*, iv., 46). Although we

* From the *Journal of the Chemical, Metallurgical, and Mining Society of South Africa*, February, 1909.

have experiments on record showing that cartridge-paper, even if intimately mixed with blasting gelatin, does not take part in the combustion when the mixture is exploded in a lead block, the conditions in a drill-hole may be different.

Here we may have the key to the whole problem before us. The assumption that the cartridge-paper takes part in the combustion would not only explain the deficiency of oxygen, the practically constant ratio of CO, and the absence of nitrogen oxide in anything like proportional quantities, but it would also furnish a reasonable explanation of the presence of hydrogen proved in the samples.

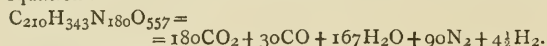
There is one more point of our subject which needs some explanation, viz., the calculation of the analytical results back to the gases formed in the drill-hole. Considering the great length of my paper, I shall attempt to be as concise as possible.

I have previously mentioned that the statement of the analytical results in the above form is, in my opinion, the only one permissible. I have not however, elaborated the fact that our knowledge of the chemical reaction taking place in the drill-hole, on which, of course, all the calculations must be based, is by no means complete and final. The results published must of necessity share this fate. For practical purposes they are, notwithstanding, near enough to justify their publication.

The calculations have been based on the consideration that the total volumes of CO₂ and CO found in the sample must necessarily be proportional to the total volume of gases which all the carbon in the explosive is capable of yielding. This ratio corresponds to the dilution of the products of explosion with air. After allowing for the amounts of CO and CO₂ which the air contains prior to the blast, and multiplying the analytical results by the dilution factor, the total quantities and, of course, also percentages of the explosion products are obtained.

It therefore only remains to decide on the actual amount of carbon taking part in the reaction. For this the chemical formula of the explosive involved has sometimes been taken as, for instance, 57C₃H₅(O.NO₂)₃.C₂₄H₂₂(NO₂OH)₉O₁₁, i.e., that of a 7½ per cent blasting gelatin. On other occasions the cartridge-paper has been stated as having taken part in the reaction, which in the case of a 7½ per cent blasting gelatin results in the formula C₂₁₀H₃₄₃N₁₈₀O₅₅₇.

From the latter I have evolved the following reaction equation:—



It is interesting to compare the composition of gases so calculated with the results of an analysis of the gases produced by blasting gelatin.—

	Analysis of sample.		Calculated to drill hole gases.	Theoretical results from above equation.
	Before blast.	After blast.		
CO . . .	0·049	0·55	7·22	9·85
CO ₂ . . .	0·356	4·64	61·78	59·11
N . . .	79·025	75·51	28·33	29·56
O . . .	20·570	19·12	—	—
H . . .	—	0·18	2·59	1·48

In the above calculations I have made use of figures showing the percentage composition of cartridge-paper as published by Dr. Moir (*Journ. Chem. Met. and Mining Soc. of South Africa*, April, 1906, vi., 307).

In conclusion, I should like to take this opportunity of acknowledging and thanking Mr. Greig for the able work and assistance which he has rendered during the whole course of these investigations.

They are not yet completed, but the results obtained so far have, I trust, been of some assistance in establishing the fact that CO in considerable quantities is present in the drill-hole gases of blasting gelatin.

APPENDIX.

Figures and data involved in analysis of gases given off by gelignite.

Determination of amount of Sample taken.—The sample

bottle after connecting with apparatus showed a temperature of 23·5° C. and 630·7 mill. barometric reading; an internal pressure of 16·0 mill. above the barometer. During the course of the analysis 12,209 grms. of mercury (S at 24·5° C. = 13·5350) equal to 902 cc. had been introduced into the same bottle. At the end of the estimation the temperature had risen to 24·5° C., the barometric pressure remaining at 630·7 mill. The original volume of the sample bottle was decreased by 902 cc., and therefore, provided that the remaining gas was brought to the same temperature and pressure conditions as existed originally in the sample bottle, this decrease corresponds to the volume of gas displaced and used. It therefore remained only to bring the gas left in the bottle by means of the aspirator to that pressure which at the changed temperature corresponds to the original condition. The formula is—

$$P_1 = P \frac{273 + t_1}{273 + t}$$

In our determination, $P_1 = 648·9$ mill.; and the pressure inside the bottle was consequently adjusted to that figure. The volume of gas taken from the sample bottle now corresponds to the volume of mercury introduced, i.e., 902 cc. at 23·5° C. and 646·7 mill. pressure, which equals 707 cc. N.T.P.

In cases where the gas samples are in a moist condition, the influence of the vapour tension due to the change in temperature must be allowed for, by adding or subtracting this difference to or from the results obtained by the above formula.

Estimation of CO by Titration of Iodine Solution with Thiosulphate of Sodium.—A freshly standardised solution of sodium thiosulphate was prepared for each analysis, containing about 5 grms. of this salt per litre. For the standardisation, freshly sublimed iodine was taken, starch being used as indicator for this as well as the actual estimations.

0·1674 grm. iodine dissolved in potassium iodide solution made up to 250 cc.

Twenty cc. of this solution equal to 0·013392 grm. iodine required 48·90 cc.

Hypo solution (mean of 3 titrations).

The iodine solutions from the analysis required:—

Before blasting . . . 3·80 cc.
After blasting . . . 71·80 "

From the equation $\text{I}_2\text{O}_5 + 5\text{CO} = \text{I}_2 + 5\text{CO}_2$, 1 grm. of iodine is liberated by 0·551833 grm., or 441·4663 cc. of CO.

Therefore we obtained:—

Before blast, 3·80 cc. = 0·45337 cc. = 0·028 vol. per cent CO.

After blast, 71·80 cc. = 8·6803 cc. = 1·228 vol. per cent CO.

Gas-volumetric Estimation in Modified Orsat Apparatus.

	cc.	°C.	cc.
Gas taken	139·85	at 21·5	= 139·85
After KOH absorption	131·85	at 21·4	= 131·18
After fuming H ₂ SO ₄	131·12	at 21·4	= 131·17
With palladium tube affixed before burning	131·15	at 21·4	= 131·20
After burning	130·19	at 21·5	= 130·19
After absorption of CO ₂ formed	128·38	at 21·5	= 128·38
After absorption of oxygen	104·23	at 21·6	= 104·20

(Pressure constant all the time).

CO₂ = 139·85 cc. — 131·18 cc. = 6·2 vol. per cent.
Olefines (nil).

CO and H = 131·19 — 128·38 — $\frac{2·80}{3}$ = 1·344 vol. per cent.

CO from iodine estimation = 1·228 vol. per cent.

H therefore = 0·116 vol. per cent.

O = 128·38 — 104·20 + 0·93 = 17·960 vol. per cent.

A REVISION OF THE ATOMIC WEIGHT OF CHROMIUM.*

FIRST PAPER.—THE ANALYSIS OF SILVER CHROMATE.

By GREGORY PAUL BAXTER, EDWARD MUELLER,
and MURRAY ARNOLD HINES.

(Concluded from p. 191).

Density of Silver Chromate.

In order to correct the weight of silver chromate to a vacuum standard, a knowledge of its specific gravity is necessary. This has already been determined by Playfair and Joule (*Mem. Chem. Soc.*, 1845, ii., 401) and Schroeder (*Liebig's Annalen*, 1874, clxxiii., 72), who obtained the value 5.77 and 5.53 respectively. On account of the marked difference between these values, new determinations of the density were made by the displacement of

The following vacuum corrections were applied:—

	Specific gravity.	Vacuum correction per grm.
Weights	8.3	—
Toluene	0.862	+0.000126
Silver chromate ..	5.625	+0.000069
Silver chloride ..	5.56	+0.000071
Silver bromide ..	6.473	+0.000041

Balance and Weights.—All weighings were made by substitution upon a nearly new short-armed Trömmner balance, easily sensitive to one-fiftieth of a mgrm. with a load of 50 grms.

The gold-plated Sartorius weights were carefully standardised by the method described by Richards (*Journ. Am. Chem. Soc.*, 1900, xxii., 144), and were used for no other work.

SERIES I.—2AgCl : Ag₂CrO₄.Ag/AgCl = 0.752632 (Richards and Wells, *Pub. Carnegie Inst.*, No. 28, 1905).

No. of analysis.	Sample of Ag ₂ CrO ₄ .	Corrected weight of Ag ₂ CrO ₄ in vacuum. Grms.	Weight of AgCl in vacuum. Grms.	Loss on fusion. Grm.	Weight of asbestos. Grm.	Dissolved AgCl from filtrate. Grm.	Corrected weight of AgCl in vacuum. Grms.	Ratio, 2AgCl : Ag ₂ CrO ₄
I.	II.	10.30985	8.90835	0.00063	0.00117	0.00019	8.90908	0.864132
2.	II.	8.26920	7.14327	0.00063	0.00211	0.00017	7.14492	0.864040
3.	IV.	6.56679	5.67324	0.00039	0.00136	0.00023	5.67444	0.864111

Average 0.864094

Per cent of Ag in Ag₂CrO₄ 65.0345SERIES II.—2AgBr : Ag₂CrO₄.Ag/AgBr = 0.574453 (Baxter, *Journ. Am. Chem. Soc.*, 1906, xxviii., 1322).

No. of analysis.	Sample of Ag ₂ CrO ₄ .	Corrected weight of Ag ₂ CrO ₄ in vacuum. Grms.	Weight of AgBr in vacuum. Grms.	Loss on fusion. Grm.	Weight of asbestos. Grm.	Weight of AgBr from filtrate. Grm.	Corrected weight of AgBr in vacuum. Grms.	Ratio, 2AgBr : Ag ₂ CrO ₄
4.	I.	2.63788	2.98579	0.00028	0.00056	0.00014	2.98621	1.13205
5.	II.	2.82753	3.20018	0.00008	0.00060	0.00014	3.20084	1.13203
6.	III.	2.33454	2.64054	0.00032	0.00220	0.00026	2.64268	1.13199
7.	I.	1.77910	2.01304	0.00050	0.00144	0.00004	2.01402	1.13204
8.	I.	2.33198	2.63988	0.00030	0.00034	0.00002	2.63994	1.13206
9.	II.	3.10402	3.51311	0.00033	0.00094	0.00018	3.51390	1.13205
10.	III.	2.92751	3.31411	0.00027	0.00033	0.00010	3.31427	1.13211
11.	III.	4.21999	4.77677	0.00055	0.00126	0.00014	4.77762	1.13214
12.	II.	5.24815	5.93939	0.00025	0.00170	0.00020	5.94104	1.13203
13.	IV.	6.24014	7.06401	0.00039	0.00104	0.00018	7.06484	1.13216
14.	IV.	7.92313	8.96913	0.00083	0.00129	0.00022	8.96982	1.13211

Average 1.13207

Per cent of Ag in Ag₂CrO₄ 65.0321Average per cent of Ag in Ag₂CrO₄ 65.0333

Sample.	2AgBr : Ag ₂ CrO ₄ .
I.	1.13205
II.	1.13204
III.	1.13208
IV.	1.13214

Sample.	2AgCl : Ag ₂ CrO ₄ .
II.	0.86409
IV.	0.86411

toluene with weighed amounts of salt. The toluene was first dried by stick soda and was then distilled. Its specific gravity at 25° referred to the water at 4° was found to be 0.86156. Great pains were taken to remove air from the chromate when covered with toluene by placing the pycnometer in an exhausted desiccator before setting.

Weight of silver chromate in vacuum. Grms.	Weight of toluene displaced in vacuum. Grm.	Density of silver chromate. 25°/4°.
5.1584	0.7898	5.628
3.6012	0.5520	5.621
Average		5.625

Discussion of Results.

In comparing the analytical results, it is to be noted first that the compositions of the different samples agree within less than one one-hundredth of 1 per cent, as the following averages show. If anything, Samples I. and II. show a somewhat lower percentage of silver than Samples III. and IV. These samples were made from ammonium chromate which contained a slight excess of chromic acid. This excess of acid accumulated in the solution during the precipitation of the silver chromate, so that the precipitate formed under distinctly acid conditions, although the acidity was not sufficient to present any danger of the formation of dichromate. Samples III. and IV., on the other hand, since they were made from potassium chromate, which is markedly hydrolysed, were formed under distinctly basic conditions, and the precipitation or occlusion of basic

* Contributions from the Chemical Laboratory of Harvard College. From the *Journal of the American Chemical Society*, xxxi., No. 5.

salts is to be feared. Such occluded basic salts would tend to raise the percentage of silver in the chromate. However, Sample IV. yielded slightly higher results than Sample III., while on account of the method of precipitation the reverse is to be expected, for Sample III. was precipitated by adding the silver nitrate to the chromate, while Sample IV. was precipitated by adding the chromate to the silver solution, the mother-liquor remaining neutral in both cases. Too much emphasis should not be laid upon the slight apparent difference in the composition of the different samples of salt, since the variations in the experiments with the same samples are as large as the differences between the samples. Hence the average result from the different samples is employed in the final calculations, all the analyses being given equal weight in each series.

In addition to the specimens of silver chromate, the preparation and analysis of which have been described, two other interesting specimens were prepared. One was formed by adding a 0.04 normal silver nitrate solution to a solution of chromic acid of similar concentration. On account of the solubility of silver chromate in nitric acid solutions, precipitation was only partial. The precipitate was washed and dried, and upon analysis was found to contain so little silver that the presence of a small proportion of dichromate was certain, a result which was hardly to be expected in the light of Sherrill's experiments.

The second sample was prepared by heating ammoniacal solutions of silver chromate in platinum vessels, the chromate being gradually precipitated as the ammonia was expelled. This material yielded somewhat irregular results, which, on the whole, indicated too high percentages of silver, and hence the presence of basic salts, a result which could have been predicted from a consideration of the conditions of preparation.

It is to be noted that Series I. and Series II. indicate percentages of silver differing by less than four-thousandths of a per cent, a highly satisfactory agreement, which indicates purity of the halogen acids employed as well as experimental accuracy.

If the percentage of silver in silver chromate is 65.0333, the molecular weight of silver chromate may be calculated from the atomic weight of silver, and from the latter value the atomic weight of chromium by difference. Since the ratio of the atomic weights of silver and oxygen is somewhat uncertain at the present time, these calculations are carried out with various possible assumed values for the atomic weight of silver, oxygen being assumed to have the value 16.000. It is to be noted that the percentage error in the determinations of the molecular weight of silver chromate is multiplied six times in the atomic weight of chromium.

If Ag = 107.93 $\text{Ag}_2\text{CrO}_4 = 331.922$ and Cr = 52.062

If Ag = 107.88 $\text{Ag}_2\text{CrO}_4 = 331.768$ and Cr = 52.008

If Ag = 107.85 $\text{Ag}_2\text{CrO}_4 = 331.676$ and Cr = 51.976

Although slightly lower than the previous investigations, these results agree with them as closely as is to be expected, most of the probable errors in earlier work tending to make the results too high.

The more important results of this research may be briefly summed up as follows:—

1. Pure silver chromate was prepared.
2. It is shown that silver chromate cannot be completely dried without decomposition.
3. The proportion of residual water was determined in salt dried at definite temperatures.
4. The specific gravity of unfused silver chromate is found to be 5.625 at 25° referred to water at 4°.
5. The per cent of silver in silver chromate is found to be 65.0333 by two closely agreeing methods.
6. With several assumed values for the atomic weight of silver referred to oxygen, the atomic weight of chromium is found to have the following values:—

If Ag = 107.93 Cr = 52.06

If Ag = 107.88 Cr = 52.01

If Ag = 107.85 Cr = 51.98

In a subsequent paper the analysis of silver dichromate is described.

We are greatly indebted to the Carnegie Institution of Washington for generous pecuniary assistance in pursuing this investigation; also to the Cyrus M. Warren Fund for Research in Harvard University for many pieces of platinum apparatus.

SOME FORMS OF FOOD ADULTERATION AND SIMPLE METHODS FOR THEIR DETECTION.*

By W. D. BIGELOW Chief of the Division of Foods,

BURTON J. HOWARD, Chief of the Microchemical Laboratory.

GENERAL DISCUSSION.

Public Opinion.

Food legislation has received much attention abroad, and the more highly civilised foreign countries have efficient food laws and enforce them rigidly. The subject of the purity of foods is more widely studied in the United States now than at any previous time. The people as a whole are better informed on the subject than ever before, and there is a constantly increasing demand for definite information. In response to a very large number of inquiries regarding the matter this bulletin has been prepared as a popular statement regarding the nature and extent of food adulteration, and includes simple tests by which the housekeeper or retail dealer may determine some of the more prevalent forms of adulteration practised.

The demand for information on this subject is now very general, and, as is often the case when public interest is deeply aroused, there is an unfortunate tendency toward exaggeration which frequently amounts to sensationalism. Such an attitude is to be deplored, and unless it is checked must sooner or later react unfavourably. It is not unusual to speak of some of our typical foods as poisoned, and of food manufacturers as poisoners. Such characterisations are unfortunate and untrue. Deleterious substances are doubtless sometimes added to foods. At the same time the word "poison" has a very strong and distinct significance, and should not be applied to any of the substances ordinarily added to foods, except in the sense that they are harmful. The word "poisoner" signifies a person who intentionally and deliberately administers an article intended to result fatally, or at least very disastrously to health.

We do not for a moment admit that any manufacturer of foods adds to his products substances which he believes will be injurious to health. There is no reason for attributing such motives to so large and important a class of our citizens, and their business sagacity in other directions precludes the possibility of shortsightedness of so serious a nature. We cannot do less than assume that manufacturers who depend for their success upon the reputation of their brands will add nothing which they believe will make their products seriously detrimental to health. It is not to their interest to shorten the lives of their customers nor to impair their appetites. We must assume that they honestly believe the products they employ to be wholesome. Therefore, in judging of the wholesomeness of preservatives and other substances added in the preparation of foods, the subject must be treated in a conservative manner, and no criminal or even dishonest motives attributed to those who differ with us on the subject.

"Adulteration" Defined.

During recent years there has been a tendency to confuse the minds of many by an incorrect use of certain words frequently used in the discussion of foods. It is the policy of some manufacturers to limit the word "adulterated" to

* Bulletin No. 100, Bureau of Chemistry, U.S. Department of Agriculture.

foods to which have been added substances of lower value than the foods themselves, with the intention of increasing the weight or volume. This limitation is certainly not justified by the English language nor by the facts, and such a restriction of the term is entirely unwarranted. The word "adulterated" properly describes a food to which any non-conditional foreign substance, not properly constituting a portion of the food, has been added. The fact that the added substance may be at times of a greater commercial value than the food itself has no bearing on the question. Conversely, the word "pure" is properly applicable to foods that are unmixed with any foreign substance. It may be wholesome or unwholesome, but this property is not indicated by the word "pure" or "adulterated." This definition is not, of course, complete. According to the laws of many of the States a food is declared to be adulterated under the following conditions:—

First, if any substance or substances have been mixed with it, so as to lower or depreciate or injuriously affect its quality, strength, or purity; second, if any inferior or cheaper substance or substances have been substituted wholly or in part for it; third, if any valuable or necessary constituent or ingredient has been wholly or in part abstracted from it; fourth, if it is an imitation of or is sold under the name of another article; fifth, if it consists wholly or in part of a diseased, decomposed, putrid, infected, tainted, or rotten animal or vegetable substance or article, whether manufactured or not, or, in the case of milk, if it is the product of a diseased animal; sixth, if it is coloured, coated, polished, or powdered, whereby damage or inferiority is concealed, or if by any means it is made to appear better or of greater value than it really is; seventh, if it contains any added substance or ingredient which is poisonous or injurious to health: *Provided*, That the provisions of this Act shall not apply to mixtures or compounds recognised as ordinary articles or ingredients of articles of food, if each and every package sold or offered for sale bear the name and address of the manufacturer, and be distinctly labelled under its own distinctive name, and in a manner so as to plainly and correctly show that it is a mixture or compound, and is not in violation with definitions fourth and seventh of this section.

The claim is made by some manufacturers that the addition of a preservative to food does not properly constitute adulteration, because the preservatives added are of greater commercial value than the foods themselves. Such a claim, however, seems to be nothing but a play upon words. For instance, benzoate of soda has a greater commercial value, weight for weight, than tomatoes, and the claim has been made that for that reason its addition to tomatoes actually increases the expense of the preparation of tomato catsup. As a matter of fact, however, it permits the tomato pulp to be prepared in large quantities and preserved in barrels in a much less expensive way than can be done without its use. It is evident, therefore, that even though the preservative employed is more expensive than the substance to which it is added, the addition is really made for the purpose of cheapening the product. It is not for this reason that such a substance is properly called an adulterant, however, but because it is an added foreign substance, and is neither a food nor a condiment. These definitions cannot be emphasised too strongly. Adulterated foods are not necessarily unwholesome foods.

The term "misbranded" is appropriately applied to foods incorrectly described by the label. The word has not the same significance as "adulterated," and yet the two terms may frequently be applied to the same product. For instance, commercial starch is sometimes added to sausage to increase its weight and permit of the use of a larger amount of water or of fatter meat than could otherwise be used. Such a product may properly be deemed adulterated, and at the same time, if the article were properly branded it might not be open to objection either on the score of unwholesomeness or adulteration. If such an article, however, be sold simply as sausage, the purchaser must

naturally assume that no substance has been added to increase the weight of the material without a corresponding increase of nutritive value. The addition of starch to sausage therefore is not in itself deleterious to health, but in the absence of a proper declaration is a fraud, because it cheapens the article which the customer supposes he is buying. In this connection, however, attention should be called to the claim of packers that 1 or 2 per cent of starch should be added to the sausage that is to be boiled, in order to prevent its shrinking when the sausage is cooked.

The following definitions of "adulteration" and "misbranding," as applied to foods, are taken from the Food Bill now pending in Congress (House of Representatives, Fifty-ninth Congress, Report No. 2118, March 7, 1906):—

Sec. 6.—That for the purposes of this Act an article shall be deemed to be adulterated—

In the case of food:—

First.—If any substance has been mixed and packed with it so as to reduce or lower or injuriously affect its quality or strength.

Second.—If any substance has been substituted wholly or in part for the article.

Third.—If any valuable constituent of the article has been wholly or in part abstracted.

Fourth.—If it be mixed, coloured, powdered, coated, or stained in a manner whereby damage or inferiority is concealed.

Fifth.—If it contain any added poisonous or other added deleterious ingredient which may render such article injurious to health: *Provided*, That when in the preparation of food products for shipment they are preserved by an external application applied in such manner that the preservative is necessarily removed mechanically, or by maceration in water, or otherwise, the provisions of this Act shall be construed as applying only when said products are ready for consumption.

Sixth.—If it consist in whole or in part of a filthy, decomposed, or putrid animal or vegetable substance, or any portion of an animal unfit for food, whether manufactured or not, or if it is a product of a diseased animal, or one that has died otherwise than by slaughter.

Sec. 7.—That the term "misbranded," as used herein, shall apply to all drugs, or articles of food, or articles which enter into the composition of food, the package or label of which shall bear any statement regarding the ingredients or substances contained in such article, which statement shall be false or misleading in any particular, and to any food or drug product which is falsely branded as to the State, Territory, or country in which it is manufactured or produced.

That for the purposes of this act an article shall also be deemed to be misbranded:—

In the case of food—

First.—If it be an imitation of or offered for sale under the distinctive name of another article.

Second.—If it be labelled or branded so as to deceive or mislead the purchaser, or purport to be a foreign product when not so.

Third.—If in package form, the quantity of the contents of the package be not plainly and correctly stated in terms of weight or measure, on the outside of the package.

Fourth.—If the package containing it or its label shall bear any statement, design, or device regarding the ingredients or the substances contained therein, which statement, design, or device shall be false or misleading in any particular: *Provided*, That an article of food which does not contain any added poisonous or deleterious ingredient shall not be deemed to be adulterated or misbranded in the following cases:—

First.—In the case of mixtures or compounds which may be now or from time to time hereafter known as articles of food, under their own distinctive names, and not an imitation or offered for sale under the distinctive name of another article, if the name be accompanied on the same

label or brand with a statement of the place where said article has been manufactured or produced.

Second.—In the case of articles labelled, branded, or tagged so as to plainly indicate that they are compounds, imitations, or blends: *Provided*, That the term blend as used herein shall be construed to mean a mixture of like substances, not excluding harmless colouring or flavouring ingredients: *And provided further*, That nothing in this Act shall be construed as requiring or compelling proprietors or manufacturers of proprietary foods which contain no unwholesome added ingredient to disclose their trade formulæ, except in so far as the provisions of this Act may require to secure freedom from adulteration or misbranding.

Chemical Preservatives.

During recent years the practice has sprung up of adding to many articles of foods certain chemical substances which have the property of delaying or preventing fermentation and decay. These substances are commonly known as chemical preservatives. Among them are salicylic, benzoic, and boric acids, and their sodium salts (sodium salicylate, sodium benzoate, and borax), formaldehyde, ammonium fluoride, sulphurous acid, and sulphites.

It is claimed by those who favour the use of chemical preservatives that the action of the latter is similar to that of salt, vinegar, and wood smoke, and that the use of the former is not open to greater objection than that of the latter. In fact, there are not wanting some who claim that the former are less objectionable than the latter. The literature regarding the wholesomeness of the so-called chemical preservatives is not by any means uniform in either approving or disapproving them. It is the opinion of this Bureau that they cannot be regarded as entirely wholesome even in the small amounts generally added to foods. The recent investigations conducted by this Bureau, in which twelve men were used as subjects, demonstrated that boric acid is injurious to health (U.S. Dept. Agr., Bureau of Chemistry, Circular No. 15 (digest), and *Bulletin* No. 84, Part I.). The experiments of the German Imperial Board of Health had the same result, and Germany has prohibited the use of this preservative altogether. It is almost universally conceded that formaldehyde and fluorides are injurious, and the weight of evidence is decidedly adverse to sulphurous acid as a preservative of meat products. The experiments of the Bureau of Chemistry indicate that neither salicylic acid nor benzoic acid is free from injurious effects.

There are now upon the market a large number of brands of commercial preservatives, and there are firms who make a specialty of preparing such preservatives. These substances are usually composed of the chemicals mentioned above. They are frequently sold with the statement that they comply with all pure-food laws, that they are entirely wholesome, and the claim is sometimes made that they are new products, and that their presence in foods cannot be detected by the chemist. These statements are all untrue. As stated above, commercial preservatives usually consist of common substances of well-known antiseptic action. Their use is forbidden in many States, and their detection is not a difficult matter.

As a result of these claims many small manufacturers are led unwittingly to violate the food laws of the various States. By using commercial preservatives which they are led to believe are not objectionable they add substances to their foods which they would not knowingly employ. Such instances have repeatedly occurred, and a number of preparations of similar nature are also put up in small packages and sold by agents from house to house for the preparation of what is known as "cold process" preserves. These preparations are sold under the claims mentioned above, and many housekeepers have been led to use them who would not have employed them had they known their true character. Unfortunately, they are sometimes accompanied by directions for the preparation of fruits without any heat whatever, and in such cases the amount of pre-

servatives employed is often far in excess of that which even the advocates of food preservatives advise.

Colouring Matter.

Some difference of opinion has arisen among hygienists regarding the wholesomeness of the substances frequently employed for colouring foods. European countries have legally recognised the wholesomeness of a considerable number of coal-tar derivatives. In this country a preference is frequently given by the State laws to vegetable colours, although coal-tar derivatives are more commonly employed.

As far as their application to the preparation of foods is concerned, coal-tar colours have been found to be much more satisfactory from a technical standpoint than the pure vegetable colours. They are readily soluble, are cheap in consideration of the amount employed, and withstand the action of light and time much better than the ordinary vegetable colours available for colouring food.

In addition to any influence on digestion and health which the coal-tar colours may have, a certain amount of arsenic is added to them by some methods of preparation. In some colours, however, prepared with a special view to use in foods, arsenic is practically or entirely absent. In this connection it must be borne in mind that the amount of colouring matter necessary to give a food the desired tint is very small, and the danger to health resulting from its use should not be exaggerated. The question of fraud, however, remains, and the use of colours enables the manufacturer to give inferior products the appearance of high-priced goods. Yet, again, the colours may be used merely to produce an appearance more attractive to the eye and in accordance with popular taste, even though the best materials were employed. Thus, colouring matter may be added to foods for any of the following reasons:— It is sometimes placed in jelly and similar preparations when made only from the more expensive fruits and sugar, to make the colour more permanent and enable the product to retain its appearance for a longer time upon the shelves of the grocer. If a considerable portion of the fruit has been replaced by means of apple juice and glucose, the colouring matter is added to simulate the appearance of the fruit that is supposed to be present. In the cheapest grade of jellies, which are made entirely from apple and glucose, and flavoured artificially to imitate the product of higher priced fruit, colouring matter is employed to represent the appearance of the product imitated.

In the preparation of tomato catsup the natural colouring matter of the tomato is largely destroyed. This destruction is not so complete if the product is promptly made as when the pulp is stored for a considerable time before it is used, long storage of the pulp bleaching it to some extent. The addition of a little colouring matter therefore has been resorted to for the purpose of imitating the colour of the product which is made promptly and by the most careful methods. The addition of colour, however, is likely to be abused, and this tendency has resulted in placing upon our market tomato catsup of a deep red colour, much more vivid than could possibly be obtained without the use of artificial colours.

In the preparation of cucumber pickles the natural green of the cucumber is somewhat impaired. Some manufacturers have employed copper compounds for the purpose of imparting to the product a greenish tint. This also has been carried to excess, and we sometimes find upon our market pickles of a bright green hue which is not suggestive of any natural food. The same practice obtains in the preparation of canned peas and beans. The great majority of those products imported from Europe are coloured with copper, and as a result are of a much brighter colour than the same vegetables cooked when gathered freshly from the garden.

In the manufacture of butter it is found that the colour varies with the season of the year, the feed of the cow from which the milk is obtained, and within certain limits with the breed of the cow. This results in a variation in the

colour of butter which manufacturers have attempted to correct by adding a sufficient amount of colouring matter to make the colour uniform. This practice has also been carried to excess, and the butter now on our market is coloured more deeply than is natural. This colour varies in different markets of the country. Fortunately, during recent years, there has been a tendency to decrease the colour of the butter, and it is to be hoped that before many years people will demand a product which is prepared without any addition of colour whatever.

Colouring matter is sometimes employed for the purpose of simulating the appearance of a more perfect article than that actually used. For instance, in the preparation of canned tomatoes a product having a certain brightness of colour may be obtained if the tomatoes are perfect, fully ripe, and of certain varieties. Often, however, the tomatoes delivered to the canner do not yield a product of the desired colour. For this reason some cannerymen make a practice of adding colouring matter to their product, thus giving it an appearance which they say is more acceptable to their customers.

Again, in the case of meat the colour disappears after considerable time, the meat losing its bright fresh colour before the process of decay is evident. Therefore, the colouring matter is not usually applied to fresh meat held at low temperature, but to chopped meat, Hamburg steaks and sausage, the addition of colouring matter to this product thus giving it the fictitious appearance of fresh meat.

(To be continued).

SOME RECENT RESULTS OF ASTRONOMICAL RESEARCH.*

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Chief Assistant in the Royal Observatory, Greenwich.

(Continued from p. 189).

Comet C 1908.

WE must now leave the system of Jupiter and turn to another subject which has been occupying attention at Greenwich, and in fact the attention of the whole astronomical world—Morehouse's comet—the comet which appeared last autumn, and which, although it has long ceased to be visible in these latitudes, is still being followed with great interest by observers in the southern hemisphere. I daresay I am speaking to some here who will remember the great comet of 1858; others will remember the comets of 1862, 1874, or 1882. I feel rather at a disadvantage in speaking of comets to you; comets nowadays are not what they used to be, and compared with these glorious wanderers, the little comet of which I have to speak made a very poor show. It will, I fear, be necessary to make out a very strong case if you are to be persuaded that this little object, which was hardly more than glimpsed with the naked eye by practised observers, and was generally considered very disappointing as seen with the telescope, is worth the attention that has been devoted to it.

Before proceeding further let me introduce the comet under consideration. Here it is as it appeared on September 30 last year. (Two photographs were thrown in succession on the screen). But I think no one could undertake to recognise it again from its photograph. Here is the same comet a day later. Everything is altered completely; you cannot point to a feature in the tail on this photograph and say that it corresponds to a certain feature on the previous photograph, and that one has changed into the other; you cannot say that this is the tail of the previous day modified. As far as can be judged the tail is an entirely new one, and if these two photographs were all the data available we might, it is true, learn something

of the mode in which the activity breaks out and dies away from day to day, but it would not be possible to trace the motions of the particles of the tail, and the most hopeful line of research by which something may be understood of the nature of the comet's tail would be closed. Now that is what has generally happened in the case of the former comets, at any rate, since it has been possible to apply powerful telescopes and the best photographic methods to the study. Most comets, and the same applies to planets and satellites, are well placed for observation for, say, three hours at a time, but the rest of the night are too close to the horizon to be satisfactorily photographed. But this comet for a month or so after its discovery chanced to be in the neighbourhood of the North Pole, so that it simply circled in a small path round the Pole during the twenty-four hours, and the whole night long from dusk to dawn it was in a favourable position for being photographed. That is the first factor which rendered this comet an important one—its exceptional position. An observatory in a high latitude like ours is generally at a great disadvantage compared with one at the equator; we, for instance, never have an opportunity of seeing Mars under really good conditions; but for once high latitude was useful.

It was very soon realised that here was an unusual opportunity for studying the processes going on in a comet, and the Astronomer Royal arranged for the taking of long series of photographs at frequent intervals, so as to obtain as it were, a cinematograph record of the changes taking place throughout the night. The weather was on the whole favourable, and several times a series of eight or nine photographs on a single night was obtained; in one case the series extended over nearly nine hours, so that there is an opportunity of following step by step the great and striking changes which the comet undergoes in that interval. Altogether the three observers, Mr. Davidson, Mr. Melotte, and Mr. Edney, by dint of constant and continuous watching obtained 200 photographs; from these are selected the photographs that are being shown on the screen to-night.

Besides its position this comet was from another point of view remarkably favourable for our purpose, namely, of studying the motions in the tail. I think that never before have photographs been obtained showing such an amount of intricate detail and such delicate and contorted streamers. This circumstance can best be appreciated by comparing this comet with others previously photographed at Greenwich under precisely similar conditions. In all our previous photographs the streamers are of a straight or gracefully curved character—never contorted, never resembling wavy locks of hair, such as the name "comet" suggests. (This statement refers to the part of the tail close to the head, which is shown in our reflector photographs). But in the present comet the tail is generally composed of fine twisting or curdled streamers; there are marks which you can seize on, set cross-wires on, and follow through from photograph to photograph. That is just what we require for purposes of investigation. A curious feature is that the head is very faint compared with other comets. It seems clear that this comet had really a very small nucleus, but that for some reason it was extraordinarily explosive, and poured out vast quantities of fine particles to form the abnormally bright tail. The comet was much brighter photographically than visually; its light was unusually strong at the violet end of the spectrum.

The part of the comet's tail which is shown on the photographs, taken with the thirty-inch mirror at Greenwich Observatory, is about a degree and a half. You can form a fair idea of what that looks like in the sky by remembering that the apparent width of the moon is half a degree; actually in miles the length of tail shown here would be about four million miles. That sounds a great length, but on suitable photographs a much greater length of tail could be traced; we have some photographs taken with an ordinary camera portrait lens on which a tail 12° long is shown—eight times as much as is shown on the photographs on the screen. As a matter of fact those

* A Discourse delivered before the Royal Institution, March 26, 1909.

taken by other observers all over the world are in general on a smaller scale than these Greenwich reflector photographs and show the outer parts of the tail; so far as I know there are no other series of photographs similar to these, which are specially adapted for studying the fine detail near the head of the comet, and what may be called the first eighth of its tail. Probably those which approach to them most nearly are some by Professor Wolf at Heidelberg, which are on half the scale. Yet one other fact I may mention; owing to the great light-gathering power of the reflector fine photographs of the comet could be obtained with quite short exposures; this is a matter of great consequence. At first we took some plates with exposures of half to three-quarters of an hour as well as shorter ones; but it was found that exposures of ten to fifteen minutes showed finer detail and were better for our purposes. This was not because the longer ones were over-exposed, but because the changes taking place within the comet are so rapid that in a thirty-minutes exposure all the fine lines and streamers become blurred.

I hope it will be understood that I mention these features of the Greenwich photographs, not with any idea of claiming that they are superior to or more important than those taken by many observers elsewhere; to do so would not do justice to the remarkable results obtained by Barnard, Wolf, and others; it is rather to show that these photographs cover new ground, and the evidence they afford and the results they lead to will be somewhat different from those elsewhere. And for the reasons already explained this is the first time it has been found possible to thoroughly examine a comet in this way. As regards the results, we are still in the midst of the work of examining the photographs, a great deal of preliminary computation had to be gone through before a serious start could be made; the measures of the details require very much comparing and digesting. By the kindness of the Astronomer Royal I am permitted to speak of them so far as we have progressed at present, but all I can say must necessarily be of a very preliminary character.

Let us first turn attention to the intermittent character of the activity of the comet. The outpouring of matter to form the tail is not at all steady, but periods of great disturbance and quiescence succeed one another at intervals of a few days. The eruption goes through stages which are more or less well defined. (A typical series of slides showing the stages of the eruption was shown).

But the great outstanding problem in the study of comets, the one on which more particularly we hope to obtain some light by the taking of this extensive series of photographs, is the study of the motions of the particles of the tail and the forces which cause them. The tail streams out from the comet in the direction nearly directly away from the sun. It is not simply left behind by the comet. It is driven away from the sun, and may be either in front or behind the head in its orbital motion according to circumstances. We are accustomed to regard the sun as the centre of an attractive force by which the planets are kept in their orbits, and comets' heads also move under the same law so far as can be ascertained. But the tail particles of the comet do not seem to recognise this force, or, at least, with them it is more than counterbalanced by a repulsion; for them the sun behaves as a centre of repulsion and urges them away. It was for long a great puzzle to understand how the sun can thus play a double rôle, but various plausible explanations are forthcoming, some of which I shall consider presently. The difficulty is now not so much to suggest an explanation as to decide between rival explanations.

A great deal of work has already been done on this subject in the case of previous comets. Of modern workers the name of Bredichin stands out pre-eminently. Much of his work was done thirty years ago—of course, derived from visual observations—but it is still of fundamental importance. By studying how much the tail lagged behind the radius vector (by the radius vector is meant the direc-

tion from the sun to the comet, which is, of course, the direction in which the solar repulsion acts), and also the curvature of the tail, Bredichin was able to form a measure of the amount of this repulsive force. It is convenient to compare this repulsion with the ordinary attractive force of gravitation of the sun in the same position (the force which the head of the comet is experiencing) and use that as a unit. It was found that the tails of comets could be divided into three classes, for which the repulsive force was respectively 1.8, 2.2 to 0.5, and 0.3 to 0 in terms of this unit. Very often a comet would have two or three distinct tails, so that all three classes might be represented in a single comet.

The introduction of photography has naturally improved the methods by which the forces may be determined. Perhaps the most remarkable researches are those of Jaegermann; he has, in the case of several comets, proved the existence of repulsive forces in just the same way that the existence of the ordinary attractive force on a planet is proved—namely, by calculating the orbit in space of the matter acted on by the force. To show how this may be done. (Two photographs of the present comet taken three hours apart were shown combined on one plate, so as to show the motion amongst the stars in that interval). The head of the comet is moving in one orbit; but there is a detached mass, which was evidently projected from the head some hours before, which is moving in a different orbit. Now, from four observations of the position of this head, we can calculate the orbit and the force exerted on it by the sun (I say four observations, and not three, because I want to determine the force exerted by the sun, and not assume it as known). Similarly, from four observations of this detached piece we might calculate its orbit and the force exerted on it by the sun. Jaegermann has examined in this way detached portions of former comets, and shown that the detached portions pursue hyperbolic orbits convex to the sun, showing that they are repelled from it.

The results of determinations of the repulsion, whether found in this way or following Bredichin's method, have generally given repulsive force according to his rule, *i.e.*, not exceeding eighteen times the attractive force of the sun; but there are two or three cases where clear evidence has been attained of a repulsive force thirty-six, and in one case, namely, the case illustrated on the screen, Jaegermann found a force of at any rate over sixty; he put it at eighty-nine.

These repulsive forces are determined from the motions of large masses of cometary matter, or from the general direction of the streaming of the tail. It is of interest to see whether the small knots or bends or bright patches, which offer a definite mark for measurement, show the same evidence of repulsion. It is necessary in pursuing this inquiry to be very careful to choose for measurement something that is a real material point. We are liable, for instance, to choose as a mark the point of crossing of two streamers; that must be avoided, for the speed of such a point is not generally that of the material of the streamers.

We have to bear in mind the distinction between the two causes of motion, an initial velocity due to explosion of the nucleus, and motion due to the action of a force; a force of repulsion from the sun produces not merely a velocity along the radius vector, but a continually increasing velocity, that is to say, an acceleration. Now one of the most important and perplexing results of studying the present comet is that there is very little evidence of acceleration, at least of the steady acceleration which would indicate a steady force. The tendency seems to be for the velocity to increase rapidly at first, but then to become constant. I showed just now two photographs in which a detached mass had broken away from the comet; it had a velocity relative to the nucleus of 2.6' per hour in the interval between those two photographs, shortly afterwards according to Professor Barnard's and our own photographs it reached a speed of 3.4' per hour, and remained constant at that for three days. There is a well-marked knot seen on photographs on October 3 which

bears every indication of being a material feature and not an allusion due to the crossing of rays. This can be traced on our photographs for six hours, during which time its distance from the head (measured in the direction of the radius vector) increases from 50,000 miles to 200,000 miles. During the first hour there is just a suspicion of an acceleration; but afterwards it moved parallel to the radius vector with a quite uniform velocity of 27,000 miles per hour (nearly eight miles a second). This is rather a good case, for there are nine photographs in the series, and the point of measurement is very well marked, but similar cases could be multiplied almost indefinitely. As soon as the distance from the head has reached a comparatively small limit, the repulsive force seems to cease. It might be suggested that the uniformity of the velocity shows that it was produced by the initial impulse, and that solar repulsion had little to do with it. But I may remind you that the way in which all the motion of the tail particles is directed nearly straight away from the sun is sufficient to assure us that a solar repulsion, and not the initial explosion, is predominant in causing the motion. The suggestion that the sun might in some way act indirectly, causing the explosion to expel the particles in the direction away from the sun, cannot be accepted; for the study of the envelopes, of which I shall speak later, indicates that, if anything, the particles are projected more abundantly towards the sun in the first instance. Besides, in the case of the knot on October 3, if we prolong backwards the uniform path we find it does not pass through the nucleus at all.

There is a curious plate taken with the portrait-lens, which, perhaps, represents something exceptional happening, but which certainly confirms the idea that the repulsion does not continue to act indefinitely. In it (shown on the screen) the tail matter is seen to be no longer streaming off, but is hanging about in a cloud and gradually diffusing.

Perhaps the simplest way of explaining this unexpected absence of acceleration is to suppose that there is some resisting material in the space, so that a limiting velocity is reached for which friction and repulsion counterbalance one another. Or we might, perhaps, suppose that the bright patches do not strictly belong to the comet, but are due to something projected from the sun, which causes a luminescence of the tail matter of the comet through which it passes. I rather lean, however, to an electrical explanation. It has been shown by various writers that the repulsion which causes the tail may be due to the action of the sun's electric field on the charged particles shot off from the disintegrating head of the comet. It seems possible that these might, after a short time, encounter particles of the opposite sign and become neutralised. Assume for the sake of definiteness that the sun has a positive charge, but is surrounded by the negative electrons shot off from it, as from all white-hot bodies, which form a swarm extending beyond the comet. Then the positive particles of the comet would be repelled, but at the same time they would be bombarded by and encounter negative electrons which might combine with and neutralise them, so that the repulsion would cease to act. I think the recombination might take place much more easily where the tail is densest, because a number of collisions would generally be necessary to capture a negative electron, so that in the fine streamers, which form the tails of ordinary comets, the repulsion might continue to act much longer. This last is a suggestion, not so much based on inherent probability, but put forward as a compromise to save us from too hastily throwing over a great deal of research and study on previous comets which has almost always assumed a constant repulsion.

(To be continued)

Lead Silicates.—Siegfried Hilpert and Paul Weiller.—When the methods of thermic analysis are applied to the investigation of the constitution of the silicates of lead it is found that lead oxide, unlike lime, forms no orthosilicate when fused with silica, but there are indications that besides the metasilicate a compound richer in SiO_2 exists. —*Berichte*, xlii., No. 13.

ON FUEL.

THE introductory lecture to the courses on "Fuel" at the Sir John Cass Technical Institute was given by Mr. J. S. S. BRAME, Lecturer on Fuel, on Monday, October 11th, when the Chair was taken by Sir BOVERTON REDWOOD, D.Sc.

The CHAIRMAN pointed out that for some time past the extension of the scope of the instruction on "Fuel" given at this Institute has been under consideration.

Hitherto there has been some work on "Fuel" included in the metallurgical courses, and there have been special courses for practical work on "Fuel Analysis" as well as in "Technical Gas Analysis," but it has been felt that in connection with the special courses for those who occupy responsible positions in industrial establishments extended instruction in the fundamentally important subject of fuel is desirable.

It would be superfluous to point out the responsibilities devolving upon all those who in various capacities are called upon to control the industrial use of fuel. Fortunately there is now a general recognition of the fact that in the matter of fuel we have in the past been disgraceful spend-thrifts, squandering our capital in such a manner that we have often obtained only a small proportion of the benefit which it is capable of giving.

We are now becoming alive to the fact that our fuel capital, solid, liquid, and gaseous, is within measurable distance of exhaustion, and that we must husband our resources if we are to avoid bankruptcy at an early date.

The cheery optimist may tell us to rest secure in the conviction that some substitute for our present fuel will be discovered in time to avert disaster, but I do not think that any of us in this room will accept that advice, or consider that it absolves us from the duty of so using what remains of our fuel as to get the highest efficiency in the shape of work with a given consumption.

Mr. BRAME took as the title for his Lecture—

"Liquid Fuel and its Economic Aspects."

He said: The use of liquid fuel for power purposes has within recent years attracted much attention in this country. It is only within comparatively recent times that great advances have been made in its utilisation in internal combustion engines, a use which has had far-reaching results. The petrol engine is, of course, a pure liquid fuel motor, and the advances directly attributable to this one form of liquid fuel include the introduction of the motor car, the submarine for naval purposes, and, lastly, led to the solving of those problems of flight which man has hoped to accomplish for many years.

As a fuel for steam-raising oils of high calorific value, cheapness and high flash-point are demanded, whilst for internal combustion engines oils of high volatility are generally requisite in order that they may readily form explosive mixtures with air in the cylinder.

For external combustion of oil fuels some spraying or "atomising" device is now practically universally adopted, some systems depending on steam injection, others on air, and another type, which is rapidly finding extended use especially for marine purposes, on the spraying action obtained through the oil being forced under pressure through suitable small orifices in the burner.

The provision of a suitable spraying burner is, however, a matter of no great difficulty. To obtain complete and smokeless combustion great attention has to be paid to the furnace arrangements, and early troubles largely arose from lack of proper attention to this point. Smokeless combustion can now be ensured.

Briefly, the advantages of liquid fuel over coal may be summarised as—superior evaporation to coal in the ratio of 1.6 to 1, ease of handling, facility it affords for stowing on ships in situations where coal could not possibly be stored, less space required than for coal, one ton of oil requiring only some 38 cubic feet, whilst coal requires some 43 cubic feet per ton. There are also numerous other minor advantages.

The many advantages of liquid fuel have created such enthusiasm in its favour that the important questions of supply and prices have frequently been overlooked.

The total oil supplies of the world, taking the figures for 1907, amounted to 34,569,500 tons, which in terms of coal, since it has such superior calorific value, would be equivalent to 51,854,250 tons of coal, or only one-fifth of the coal output of this country alone. Further, but a portion of the crude petroleum is suitable for fuel. Liquid fuel, therefore, cannot compete with coal, and is not a fuel for general use, but for employment in special cases. For naval purposes most Powers are now following the lead given by Great Britain in its adoption.

For use in internal combustion engines the lighter petroleum distillates are almost universally employed. Our annual importation of petrol has now reached the total of some 33,500,000 gallons. By the introduction of the spray carburettor a heavier grade of petrol can now be utilised, a factor of considerable economic importance as regards supplies. Further, since the calorific value of petrols of varying gravity is practically the same per unit weight (20,000 British thermal units), it follows that, as they are bought by volume, the heavier grades are more economical.

Paraffin-driven motors are valuable engines for many purposes, notably where a portable engine is required, or for boats where safety is a factor of great importance. Paraffin engines work best at constant speeds, and are not suitable for cars. One important point with all engines using petroleum oils is that high compressions are out of the question, since at little over 4.5 atmospheres there is a risk of premature ignition, hence the efficiencies obtained are low.

As petrol substitutes the claims of benzene (or benzol) and alcohol must be considered. Benzene is produced in very large quantities from both gas and coke-oven tar, and its present price is low, about sixpence halfpenny per gallon. The calorific value per unit weight is 18,540 British thermal units, but per unit volume, owing to its higher gravity, it has a higher value than many petrols.

In practice benzol gives most excellent results without any special alteration of the carburettor designed for petrol, a 40 horse-power 6 cylinder Napier having covered 22.65 miles per gallon of benzol as against 18.14 miles on petrol. Slight trouble may be anticipated in very cold weather, but usually there is no difficulty in starting the engine if a little petrol is first got through the carburettor.

Alcohol, the only fuel which we can actually manufacture from materials derived from other sources than coal, peat, or petroleum, is of special interest. The importance of alcohol and the great aid which its production on a large scale would give to agriculture, has led to the possibilities of its use being carefully studied by Commissions in Germany, France, and America.

For motor use it has many advantages over petrol or benzene; it is far less inflammable, and if a fire does arise, it can more easily be extinguished; its combustion leaves no evil-smelling products; engines run more quietly on alcohol, and it will stand higher compressions in the cylinder, thereby giving such greater efficiency that the effect of its low calorific value is almost counterbalanced.

For equal weights the calorific value of petrol to alcohol is 20,000 to 11,000 British thermal units, a ratio of 1.8 to 1, but if considered by volume the ratio is reduced to 1.6 to 1. Since the thermal efficiency of alcohol is greater than that of petrol in the ratio of 3 to 2, it is evident that volume for volume the same power can be obtained from alcohol as from petrol.

At present the cost of alcohol is prohibitive, and although in seasons when a heavy yield of raw material—chiefly potatoes—is obtained, the cost of production is comparatively low, yet with charges such as are necessarily imposed through Revenue supervision, quite independent of duty, it is unlikely that it can for many years reach the position of a commercial fuel. As pointed out by Prof.

Lewes, for use in submarines alcohol would be an ideal fluid on account of its great safety, and, in order to obtain all possible security for those engaged on this dangerous duty, expense is a matter of very minor importance.

The courses on Fuel, which include lectures on Liquid, Gaseous, and Solid Fuel, and courses of laboratory work on Fuel Analysis and Technical Gas Analysis, commenced on Monday, October 18th. Full details of the classes may be had on application at the Institute.

NOTICES OF BOOKS.

An Introduction to Physical Science. By FREDERICK H. GETMANN, Ph.D. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1909.

THIS little book is intended to provide students of chemistry with sufficient information relating to the laws of physics to enable them to read discussions of theoretical chemistry intelligently, and to interpret the results of experiments correctly. There can be no question that the facts mentioned in the book should be perfectly familiar to every student of chemistry, though possibly it would be better for him to acquire such knowledge by a thorough and systematic study of each branch of physics. Still from two points of view there is something to be said for the book. In the first place, it will save a large proportion of the time which would have to be spent in such study; and, secondly, there are certain aspects or branches of the subject which the chemist requires treated in rather fuller detail than their general importance might warrant in an ordinary elementary text-book of physics. Hence a book written specially for him is more suitable for his use than a general treatise. This book deals with mechanics, heat and light, and electricity and magnetism, and pays particular attention to phenomena and laws which are of importance in chemistry, such as, for instance, plane polarisation. It contains very good sets of questions and problems, which are not too easy but require thought and reasoning power for their solution, and also descriptions of a great number of simple experiments to illustrate the text.

Metropolitan Borough of Poplar. Annual Report for the Year 1908. By FREDK. WM. ALEXANDER, Medical Officer of Health.

THOSE who are interested in the question of disinfectants will find an interesting account in this report of the electrolytic disinfectant magnesium hypochlorite, manufactured by the Public Health Department. The figures relating to its efficacy are very striking, and the cost of production is, moreover, so low that there is a very considerable saving effected by its use. The bacteriological action of the fluid shows that it is very powerful and reliable, while it appears to be extraordinarily stable, judging from the results of determinations of chlorine more than two and a-half years after the sample was made.

Die Glasindustrie in Jena. ("The Glass Industry in Jena"). By Dr. ZSCHIMMER. Jena: Eugen Diederichs. 1909.

THIS interesting volume has been written by Dr. Zschimmer on the occasion and in commemoration of the twentieth-fifth anniversary of the founding of the Jena Glass Works by Messrs. Schott and Co., whose products are well known all over the scientific world. Although naturally it will be most appreciated by those who are connected with the great firm, it contains much that is of interest to a wider circle of readers, as, for instance, the accounts of the development of the glass industry and of the operations involved in the preparation of different kinds of glass. The descriptions of the Jena Glass Works are followed by interesting discussions of the nature of glass and the connection be-

tween its physical and chemical properties, while the many problems connected with the industry which still remain to be solved are pointed out.

Dynamik der Oberflächen. ("Dynamics of Surfaces"). By Prof. Dr. Med. LEONOR MICHAELIS. Dresden: Theodor Steinkopff. 1909.

THE important bearing of the forces localised at the surface of liquids upon biological processes is becoming more fully recognised at any rate by one, and that an influential, school of biologists of the present day, and this book aims at giving a review of the present state of our knowledge of surface forces. The first part deals with the surface considered as the seat of mechanical forces, and gives a simple and clear exposition of surface tension and energy. Methods of determining the absolute value of surface tension are described, and the results obtained for many important liquids are tabulated. Adsorption and its consequences are treated fairly fully, but there are some omissions of mention of important work, for instance, Lagergren's experiments on the phenomena of adsorption in aqueous solutions are passed over, and throughout the book the references to other authorities are rather scanty. The surface considered as the seat of electrical forces is the subject of the second part of the book, in which questions relating to potential differences, mechanical adsorption of electrolytes are discussed. The connection between electrical potential difference and surface tension is well treated, and the whole book gives an excellent introduction to the study of surface forces, more particularly from a biological point of view.

Die Elektrochemischen Verfahren der Chemischen Gross-Industrie. ("The Electrochemical Processes of Chemical Manufacturing Industry"). By Dr. JEAN BILLITER. Volume I. Halle-a.-S.: Wilhelm Knapp. 1909.

THE principles and practice of electrochemical methods of obtaining metals from their aqueous solutions and purifying them are described in this book, which is the first of four similar volumes on technical electrochemistry. It contains an introduction dealing with the theory of electrolysis, and explaining in the shortest and most concise way possible modern views as to the nature of electrochemical processes, and then treats individually those metals which are commonly prepared or purified in aqueous solution. Every care has been taken to select for description only processes which are practically employed and are found satisfactory, and although this has entailed excluding many methods which have been suggested and which may possibly prove useful, the value of the book is thus considerably increased for the practical man who wishes to study what has been, rather than what may be, done. The metals treated of include copper, silver, lead, gold, platinum, zinc, and nickel, and chapters are added on the electrolytic purification of tin and tin-plating, and on some miscellaneous processes such as the purification of bismuth and cadmium, and electrolysis with soluble electrodes for the purpose of obtaining compounds of the metals. The book will be heartily welcomed by those who are in want of a general summary of electrometallurgy rather than a comprehensive treatise on the subject, and the appearance of the other volumes will be awaited with interest.

J. and A. Churchill's Illustrated Catalogue, October, 1909.

THE latest catalogue of medical and scientific works published by Messrs. J. and A. Churchill contains many excellent specimen illustrations reproduced from the books listed, concerning which full information is given, frequently with extracts from the prefaces. In the case of fresh editions press notices are also included, and the catalogue is well arranged for purposes of rapid reference.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlix., No. 6, August 9, 1909.

Rapid Method of Determining Metallic Aluminium.—E. Kohn-Abrest.—When metallic aluminium is heated to about 300°, first in a current of hydrogen and then in a current of hydrochloric acid gas, a residue is left consisting of aluminium oxide, iron, chlorine, and different impurities, while a sublimate of aluminium chloride is obtained, containing very small proportions of iron perchloride and traces of ammonium chloride due to the decomposition of ammonium nitrate by the hydrochloric acid. Any silicon is volatilised and carried away by the current of gas in the form of silicochloroform. If the chlorine is determined in the aluminium chloride the amount of metallic aluminium is obtained directly. Special precautions have to be taken in the condensation of the vapours and their solution in water. This method enables very rapid determinations to be made of metallic aluminium and the oxide. By also estimating the silicon and the iron a complete analysis of the commercial metal can be made.

Benzidination in the Diphenyl, Diphenylmethane, and Diphenylethane Series.—H. Duval.—When the action of benzidination agents on hydrazoic derivatives of the diphenyl, diphenylmethane, and diphenylethane series is investigated, it is found that the derivatives of diphenyl behave in a peculiar way, being unaffected by stannous chloride and by boiling hydrochloric acid. In all other cases stannous chloride yields the amine derivative. When boiling hydrochloric acid acts on members of these series, if the substituting group in the nucleus is electropositive, an acridine derivative is obtained, and if electropositive no acridine is formed, but the substance is oxidised, giving an azoic compound.

Ethyl Acetal of Tetrolic Aldehyde.—P. L. Viguiet.—Crotonic aldehyde readily fixes bromine, giving dibromobutyric aldehyde, $\text{CH}_3\text{—CHBr—CHBr—CHO}$, which may be converted into acetal by Claisen's method. The removal of one molecule of hydrobromic acid by means of sodium gives dibromocrotonic acetal, $\text{C}_3\text{H}_4\text{Br—CH(OC}_2\text{H}_5)_2$, but the removal of the second is effected with difficulty, the product being tetrolic acetal, $\text{CH}_3\text{—C}\equiv\text{C—CH(OC}_2\text{H}_5)_2$.

No. 7, August 17, 1909.

Synthesis of Unsaturated Fatty Acetones.—F. Bodroux and F. Taboury.—The acetones of the fatty series which contain the group —CO—CH_3 in their molecule attack calcium carbide at their boiling-point, giving unsaturated acetones by condensation and elimination of water. With propanone the reaction begins at the ordinary temperature. It occurs very rapidly, and yields oxide of mesityl, isophorone, xylitone, and higher products of no definite boiling-points. Butanone is transformed into an acetone of constitutional formula $\text{CH}_3\text{—CH}_2\text{—C}=\text{CH—CO—CH}_2\text{—CH}_3$

CH_3

No. 8, August 23, 1909.

This number contains no chemical matter.

No. 9, August 30, 1909.

Hydrolytic Dissociation of Bismuth Iodide.—René D ubrisay.—A rise of temperature increases the dissociation

of bismuth iodide by water. Two oxyiodides appear to exist, one black and the other red, the formula of the latter being BiOI , and of the former $\text{Bi}_2\text{O}_3 \cdot 5\text{HI}$. The brick-red oxyiodide is formed when the concentration of the liquid is low, and the black substance when it is higher.

No. 10, September 6, 1909.

Calorimetric and Cryoscopic Constants of Mercuric Bromide.—M. Guichant.—The specific heat of solid mercuric bromide from 0 — 206° is 0.052 ; the latent heat of fusion at 235° is 21.8 , and the specific heat of the fused substance from 247 — 293° is 0.068 . Hence the cryoscopic constant is calculated to be $K=403$. The values found experimentally for the cryoscopic constant are considerably lower, the mean value being 340 .

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xlii., No. 12, 1909.

Indirect Titrimetric Determination of Chromium, Copper, Nickel, Cobalt, Zinc, and Lead.—A. Bacovescu and E. Vlahuta.—If solutions of soluble salts of Cr, Cu, Ni, Co, Zn, or Pb are treated with a small excess of freshly precipitated manganese carbonate, chromium is precipitated as hydroxide and the other metals as carbonates, while simultaneously an equivalent amount of manganese is set free as a soluble salt according to the equation $2\text{MnCO}_3 + \text{CuSO}_4 = \text{MnCO}_3 + \text{CuCO}_3 + \text{MnSO}_4$. By filtering off the excess of manganese carbonate and the copper carbonate and washing, the manganese sulphate can be separated and determined titrimetrically. Hence the amount of copper, chromium, &c., can be calculated. If the original solution is too acid it must be neutralised very cautiously with dilute caustic soda until a slight precipitate is obtained; this is then dissolved by warming with the necessary amount of very dilute hydrochloric acid. To determine the manganese titrimetrically it is best to use the Guyard-Volhard method, the equation of which is $3\text{MnSO}_4 + 2\text{KMnO}_4 = 2\text{SO}_3 + \text{K}_2\text{SO}_4 + 5\text{MnO}_2$.

Alkalimetric Determination of Hydroxylamine.—Arthur Stähler.—Purified hydroxylamine hydrochloride is dissolved in water, and strongly acid titanium trichloride (or sesquisulphate) solution is added till a faint pink coloration remains after shaking. The ammonia thus formed is distilled off and received into a known volume of $\text{N}/10$ acid. This method can be used to determine all organic nitrogen-oxygen compounds (hydroxylamine, oximes, nitro- and nitroso-bodies) which are converted by trivalent titanium into volatile amines which can be titrated with acids.

Hydration of Hydrocarbons of the Acetylene Series by Cadmium, Zinc, and Magnesium Salts.—M. G. Kutscheroff.—When hydrocarbons of the acetylene series are treated with halogen compounds (except iodine compounds) of mercury or magnesium, aldehydes or ketones are formed according to the constitution of the hydrocarbon. Zinc and cadmium also react similarly, but require higher temperatures. Isopropylacetylene is thus converted quantitatively into propylmethyl ketone at 150° , $(\text{CH}_3)_2\text{CH}.\text{C}.\text{CH} + \text{H}_2\text{O} = (\text{CH}_3)_2\text{CH}.\text{COCH}_3$. Apparently no intermediate metal organic derivatives are formed, the reaction being simply a hydrolysis. The ease with which hydration occurs is directly dependent upon the magnitude of the atomic weight of the metallic element. Thus with isopropylacetylene the reaction occurs at 100° with mercury salts, partially at 130° with zinc and cadmium salts (the least result being obtained with zinc salts), and completely at 150° with cadmium salts.

Guanidine Perchromate.—K. A. Hofmann and K. Buchner.—Guanidine carbonate gives with chromic acid anhydride and hydrogen peroxide a perchromate of formula $\text{CrO}_8\text{H}_3 \cdot \text{C}_3\text{N}_5\text{H}_{15} \cdot \text{H}_2\text{O}$. It forms brownish yellow prisms,

which can be kept in a dry state for weeks and are not explosive. It dissolves in water, and its solution when boiled gives up oxygen and leaves a yellow solution of guanidine chromate. When treated with ether and acidified an intensely blue coloured ethereal solution of perchromic acid, CrO_5H , is obtained. From its reactions it may be concluded that guanidine perchromate belongs to the class of red perchromates for the acid of which Riesenfeld gave the constitutional formula $\text{O}_2 : \text{Cr} : (\text{O}_2\text{H})_3$ with heptavalent chromium.

Determination of Molecular Weight by the Boiling-point Method.—Richard Meyer and Kurt Desamari.—In order to explain the difference in the results obtained in the determination of the molecular weight of tribromoresorquinone by the boiling-point method, using benzene as solvent, the authors determined the boiling-point of the pure solvent before and after the experiment. They obtained the values 79.400° and 79.425° respectively. This difference, which would have a great influence on the result obtained in the molecular weight experiment, the value calculated being 561 in the first place and 841 in the second, can only be explained by supposing that the barometric pressure varied during the experiment. To confirm this conclusion, further determinations were performed, and it was found that it is essential to apply corrections for barometric pressure. In the case of tetrabromoresorcin the result obtained when the correction was not applied was twice the true molecular weight.

Preparation and Properties of Solid Phosphorus Hydride, P_{12}H_6 .—Alfred Stock, Willy Böttcher, and Walter Lenger.—Solid phosphorus hydride can be prepared by decomposing P_2H_4 by means of dry granular calcium chloride. The P_2H_4 is prepared by allowing water to act upon calcium phosphide. When freshly prepared the phosphide is a canary yellow odourless amorphous powder with no action on litmus. It acquires an acid reaction when left in air, and then smells of phosphine. It is rapidly decomposed by light, a spontaneously inflammable gas being generated. It is insoluble in all the solvents tried, except liquid phosphorus hydride and fused phosphorus. Its physiological effects are due to the gradual evolution of phosphine.

New Solid Phosphorus Hydride, P_9H_2 , and Action of Ammonia on both Solid Hydrides.—Alfred Stock, Willy Böttcher, and Walter Lenger.—When yellow P_{12}H_6 is heated to temperatures below 200° perfectly pure phosphine is evolved; the gas is not spontaneously inflammable. The residue left is an orange-red solid hydride of formula P_9H_2 , and the simplest equation expressing its formation is $5\text{P}_{12}\text{H}_6 = 6\text{P}_9\text{H}_2 + 6\text{PH}_3$. P_9H_2 is stable in dry air, but is converted into phosphine and phosphoric acid by the action of water. It is not attacked by cold water or dilute acids, but is oxidised by strong nitric acid. The same substance is obtained when liquid ammonia acts on P_{12}H_6 , PH_3 being also generated. With liquid ammonia P_9H_2 gives a red, probably colloidal, solution which on evaporation leaves a black residue consisting of a compound of P_9H_2 and ammonia, having the character of a salt. The composition of this salt varies, the values obtained on analysis lying between those given by the formulæ $\text{P}_9\text{H}_2 \cdot \text{NH}_3$ and $(\text{P}_9\text{H}_2)_2 \cdot \text{NH}_3$. By warming the black substance or by treating it with acids, the P_9H_2 is regenerated unchanged.

The Sun as a Source of Heat in Chemical Experiments.—Alfred Stock and Hans Heynemann.—If a lens is arranged so that its focus is situated in an absolute vacuum, the heat of the sun's rays can be used to produce new and interesting results. By using a small lens and carrying out the experiments on a small scale, the authors have fused specimens of crystallised silicon (m.p. 1450°) in a few seconds, while copper and cast-iron volatilise rapidly. In repeating these experiments on a large scale the authors intend to replace the lens by a concave mirror, which will be cheaper and will absorb less heat.

THE CHEMICAL NEWS.

Vol C., No. 2605.

A SIMPLE MECHANICAL STIRRER.

By DOUGLAS H. B. COUMAN.

THE ACTION OF RADIIUM EMANATION UPON THE ELEMENTS OF THE CARBON GROUP.

By Sir WILLIAM RAMSAY and FRANCIS L. USHER.

AT the end of March one of us communicated to the Chemical Society some results dealing with this subject (*Trans.*, xcv., 624). As we have continued the investigations we think it advisable to give here the results of our experiments.

The experimental method was as follows:—The emanation was pumped, together with the accompanying detonating gas, out of a solution of radium bromide containing 0.2111 grm. of metallic radium. The gas produced in the course of a week amounted to almost exactly 25 cc. and contained 0.0912 cc. of emanation. After the explosion about half a cc. remained over; this was collected in a little glass tube coated with fused and damped caustic potash. After an hour the gas, free from carbon dioxide, was introduced into an exhausted glass flask containing the solution which was to be subjected to the action of the emanation. As the half duration of life of the emanation

HAVING recently devised a mechanical stirring apparatus which may be perhaps novel, a description may be of use to your readers.

A is a cylindrical copper boiler (1 litre) to which are soldered brass tubes, B and C, 20 cm. long; these support a piece of wide brass tubing, D, which is fitted with a cork through which a glass collar, E, is vertically fixed. F is the stirring rod enlarged to a smooth disc at G; before bending at H the glass collar, E, is slipped over the rod. K is a circular cork, being 5 cm. diameter and 1 cm. thick. It carries a number of vanes of zinc plate $\frac{1}{2}$ mm. thick, and projecting from the cork about 1 sq. cm. The vanes are inserted into slits made in the cork by means of a razor; they should be placed about 1 cm. apart around the circumference, at an angle of 30° with the vertical, so that the steam from the glass pipe, M, will exert a lifting as well as a rotating force, thus diminishing friction at O. The adjustment is most conveniently made by altering the shape and jet of the glass pipe, M. My own jet is inclined upwards, the vanes passing directly over it, and has an internal diameter of rather less than 1 mm.

N is a piece of string which holds the glass tube in a slightly strained position and diminishes its vibrations.

Using a Barthel spirit-lamp steam is ejected with enough force to rotate the stirrer rapidly in a 50 per cent solution of sugar. No lubricant is required. Steam does not con-

TABLE I.

Solution.	Vol. of emanation. Cc.	N ₂ . Cc.	O ₂ . Cc.	CO ₂ . Cc.	CO. Cc.	Detonating gas. Cc.	H ₂ . Cc.
H ₂ SiF ₆ .aq	0.0724	—	—	0.0063	—	9.15	1.03
Ti(SO ₄) ₂ .aq (a)	0.0912	0.210	—	0.054	0.096	—	0.69
Zr(NO ₃) ₄ .aq (a)	0.0692	0.762	—	0.116	0.008	—	—
	0.0865	0.456	—	0.124	0.002	—	—
	0.1120	3.686	—	0.551	—	—	—
Th(NO ₃) ₄ .aq (a) (b) .. .	0.0765	0.639	—	0.124	—	—	—
	0.0649	—	2.655	0.007	0.006	2.531	—

(a) The nitrates always give nitric oxide, which was absorbed by mercury after the addition of an unknown amount of oxygen before the analyses were performed.

(b) In this case the estimate for the amount of emanation is probably too high.

is 3.86 days, the contents of the flask were left for four weeks; after this time the energy of the emanation was almost exhausted. The gases were then pumped out and analysed. Table I. gives the results of the experiments.

In Table II. the results are arranged in such a way that the amount of carbon which is produced by a cubic millimetre of emanation is given.

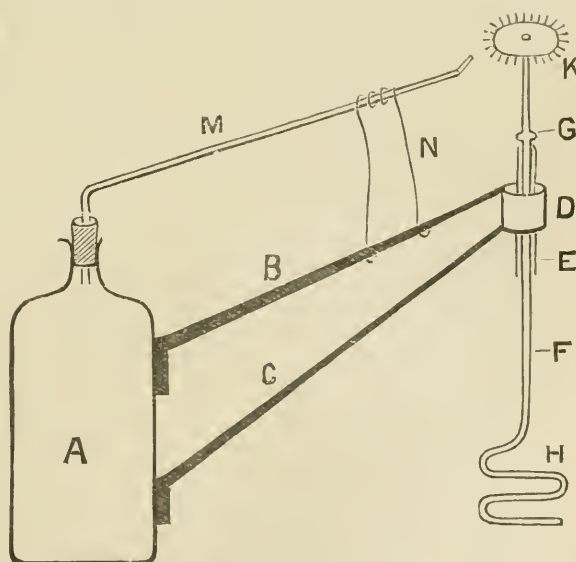
TABLE II.

Solution of—	Carbon (mgrms.).
H ₂ SiF ₆	0.518
Ti(SO ₄) ₂	0.982
Zr(NO ₃) ₄ { I. .. .	1.071
	0.873
Th(NO ₃) ₄ { I. .. .	2.93
	0.968
Pb(ClO ₃) ₂	0.102

It may be mentioned that mercurous nitrate gives no trace of carbon dioxide or monoxide.

From the figures it is seen that the elements of the carbon group, without exception, give carbon compounds when the emanation acts upon them; the amounts produced, however, are not all the same. It is not improbable that those elements which have a high atomic weight are generally more easily split up than those with lower atomic weights, but it must be supposed that lead is specially stable, and shows but little tendency to change into carbon.

Similar experiments are being performed with compounds of other elements.—*Berichte*, xlii., 2930.



dense on the vanes, and does not interfere with the liquid which is being stirred.

A safety valve would be an obvious improvement.

ANALYSIS OF THE *VEBERNUM DENTATUM*.

By CHARLES R. BLAKE.

The *Vebernum dentatum*, or arrow-wood berries, were gathered about August 20, 1906, near Sylvan Beach, New York, on sandy soil, formerly an old lake bottom.

Description.—The berries grow on bushes five to eight feet high, and are dark blue in colour and oblong in shape. The average weight is 0.03 of a gram. An analysis of the berry showed it to contain three separate parts:—(1) A thin blue-black husk, greatly wrinkled; (2) a hard yellow shell; and (3) a yellow meat or nutlet. The taste of the berry resembled that of hazel nuts, and then passed to that of coffee, except that there is also a slightly bitter taste.

The Sugars.—Fifty grms. of the uncrushed berries were placed in a litre flask fitted with an inverted condenser, to which was added a large amount of alcohol. The flask and contents were heated for several hours, and the alcoholic solution became a beautiful wine colour. This solution was withdrawn and found to contain a dirty grey sediment. The process of adding successive portions of alcohol, heating, and withdrawing was continued until the solution was no longer coloured. Since the alcohol could extract nothing more from the berries, distilled water was used. The effect was somewhat unexpected. We received a larger extraction from the berries with one application of the distilled water than we had obtained altogether with the alcohol. The total amount of the coloured solution, which was placed in a litre flask and corked, measured 606 cm. The solution had a brownish colour and gave off a sweet odour. The percentage of sugars contained in this solution was determined by means of Fehling's solution of such a strength that 10 cc. corresponded to 0.05 gram of sugar. The determination was made after the following manner:—

1 cc. of the sugar extraction was diluted with 50 cc. of distilled water in a small beaker. This was heated to boiling and titrated with Fehling's solution. To ascertain the "end-point," a small portion of the solution was filtered from time to time, always pouring the filtrate back until the sugars had no more reducing power. When the reduction was complete the solution had a greenish blue colour. The solution contained 35.74 per cent of sugar, which corresponded closely to the loss in weight of the normal fruit. In this case some allowance must be made for the loss of sugar caused by fermentation. In order to determine the particular kind of sugar present, 100 cc. of the brownish solution was purified by digesting on a water-bath with bone-black and distilled water for eight hours. After this the bone-black was removed by filtration and the filtrate was evaporated to a very small quantity on the water-bath. It was in the form of a thick viscous syrup, reddish brown in colour, and gave off a sweet odour. At no time did it give any appearance of crystallisation. Following a process according to Sherman and Williams (*Journ. Am. Chem. Soc.*, 1906, xxviii., 629) the osazone test for sugars was made. 0.01 gram of the purified sugars, 0.04 gram phenylhydrazine, 0.03 gram sodium acetate, and 2 cc. of distilled water were placed in a test-tube, lightly corked, and held in boiling water. The precipitate formed, which was yellow and flocculent, pointed to fructose. The precipitate formed in from forty-five to fifty-five seconds. Several tests were made, always with the same results.

Cobalt Nitrate.—One further test was made to determine the sugars. The cobalt nitrate test as described in Leffman and Beam on "Food Analysis," p. 110, was tried. With portions of 15 cc. of the sugar solution, 5 cc. of a 5 per cent solution of $\text{CO}(\text{NO}_3)_2$, and 2 cc. of a 25 per cent solution of NaOH , the test pointed directly to dextrose. The precipitate was a turquoise blue.

Manganese and Chromium.—It was noticed that in the process of ashing a quantity of the berries a green-coloured substance was formed in the platinum dish. This was thought to be manganese, and was determined colori-

metrically. A known amount of the crushed berries was ashed in a platinum dish and dissolved in 5 cc. of nitric acid. This solution was then transferred to a test-tube, to which was added 5 cc. of a solution of $\text{K}_2\text{S}_2\text{O}_8$. The tube was then filled to the 15 cc. mark with distilled water, heated, corked, and let cool. The solution in the tube was a beautiful wine colour. This was known as the standard tube. Seven other tubes were prepared with the same proportion of HNO_3 , AgNO_3 , and $\text{K}_2\text{S}_2\text{O}_8$ as contained in the standard tube. To each of seven tubes was added a different amount of KMnO_4 solution of known strength. In tube No. 1, 4 cc.; in No. 2, 4½ cc.; in No. 3, 5 cc., &c., until No. 7 contained 7 cc. of KMnO_4 . Finally, the seven test-tubes were filled to the 15 cc. mark with distilled water and corked. Then it was an easy matter to determine which of the seven tubes matched the colour of the standard tube. In this case the tube containing 6½ cc. of KMnO_4 matched perfectly, and the amount of Mn was 0.46 per cent. The standard tube containing the ash was then treated with 1 cc. hydrogen peroxide, and the blue tinge matched the blue colour in a test-tube prepared similarly but having 0.4 cc. of a solution of potassium bichromate. The amount of chromium determined was 0.01 per cent.

Nitrogen.—The Kjeldahl method was used in this determination. 3 grms. of the uncrushed berries were heated to boiling in 25 cc. of concentrated sulphuric acid. The amount of nitrogen present was 0.93 per cent.

The Proteins.—A small amount of the berries was crushed and boiled in distilled water for a short time. The colour of the solution was a beautiful dark wine. A small quantity was filtered into a test-tube and heated with nitric acid. A brownish yellow colour resulted with flocculent particles, and upon adding ammonia the colour changed to a reddish brown, showing the presence of albumen. Another portion of the crushed berries was placed in a dry test-tube and treated with caustic soda solution. The colour immediately turned blue, and upon heating a purple colour, giving the odour of newly made soap. The fumes reacted alkaline.

Another portion of the solution from the crushed berries was tested for sulphur. A solution of lead acetate was treated with caustic soda until the precipitate which was first formed was re-dissolved. The fruit solution was now added to this and boiled. A dark coloured precipitate of lead sulphide resulted, showing the presence of sulphur.

The Acids.—The alcohol was removed from a small amount of the unpurified solution of the sugars, diluted with water, and then tested for the acids. Tests for acetic, tartaric, and oxalic gave negative results, but tannic acid was very strong. Malic acid was also found to be present.

Cobalt.—Whenever the ash from a known amount of the berries was treated either with concentrated hydrochloric or nitric acid, the ash solution immediately changed to a beautiful pink colour, indicating that there might be a trace of cobalt present. Therefore a portion of the ash was tested for cobalt according to Treadwell-Hall's method, page 137. Our test showed that not even a trace of cobalt was present.

The Ash.—Four portions of berries were weighed out into a platinum dish, and heated with a free flame until nearly all the organic matter was consumed, leaving a dark grey ash. The odour given off was similar to that of roasted coffee. From one portion of the berries the silica, iron, calcium, aluminum, and magnesium were determined; from another portion the alkalis; from another portion the sulphate; and, finally, the phosphate. For the first we took 3.508 grms. of the berries and received 0.0860 gram of ash, or 2.16 per cent. The result of the analysis is given in the table (see next column).

The amount of CO_2 and some unburned organic matter in each case was not determined.

Oils.—The nutlets from which the sugars were extracted were now tested for the oils. The berries were crushed and weighed 61 grms. in all, and then treated with ether. They were heated on the water-bath in an open flask for

	Per cent of ash.
Fe ₂ O ₃	0.41
Al ₂ O ₃	27.83
K ₂ O	13.22
Na ₂ O	15.82
P ₂ O ₅	1.30
MgSO ₄	4.50
MgCO ₃	6.24
CaCO ₃	23.05
Mn ₂ O ₃	0.84
Cr ₂ O ₃	0.28
Total	93.49

twelve hours. The liquid was filtered off, which contained a large per cent of ether and oils. This liquid was distilled, and we obtained two distinct oils, a clear one and a dark green coloured one. In spite of the presence of ether the oil gave off a rich nutty odour. The berries were treated in the above manner until there was only one oil that came off. For some time a greenish oil came off with the clear oil, but upon separation the clear oil evaporated at once. The residue was a brownish sediment, and had a rich hazel-nut odour. After standing for some time it gave off an odour of maple syrup. The dark green oil was quite heavy and somewhat viscous. None of the oil ever crystallised.

To determine this green coloured oil it was saponified in the following manner:—One grm. of the oil was weighed out on a watch-glass. This was transferred to a 16 oz. flask, and 10 cc. of semi-normal solution of KOH in alcohol was added. This mixture was heated on the water-bath for about half an hour or until the fat globules had dissolved. 1 cc. of an alcoholic solution of phenolphthalein was added, and then titrated with a semi-normal solution of HCl.

Then to cc. of KOH was titrated in the same manner. The difference between the volumes of the semi-normal HCl solutions used in both cases gives the number of cc. corresponding to the alkali neutralised in saponifying the oil. Each cc. of semi-normal HCl used represents 0.002805 of KOH. Hence the percentage of KOH required to saponify can be readily ascertained. To find the saponification equivalent divide the weight of the sample employed (expressed in mgrms.) by the number of cc. of normal acid corresponding to the alkali neutralised by the oil. Figuring from known weights of oil corresponding very nearly to the substance known as *Laurin*, below is the recorded result:—

Substance : *Laurin*.

Chief Source : *Cocoa-nut and Palm-nut Oil*.

Percentage of KOH required ..	26.38	24.68
Saponification equivalent . . .	212.67	227.27

I wish to express my thanks to Dr. N. Knight for his many timely suggestions in this piece of research work.

Cornell College, Mt. Vernon, Iowa.
September 30, 1909.

SOME RECENT RESULTS OF ASTRONOMICAL RESEARCH.*

By ARTHUR STANLEY EDDINGTON, M.A., M.Sc., F.R.A.S.,
Chief Assistant in the Royal Observatory, Greenwich.

(Concluded from p. 205).

OF the various theories that have been put forward in order to account for the repulsion of comets' tails, besides the electrical theories, probably the most popular is that which ascribes the streaming away from the sun to the effect of light-pressure. When radiation of any kind, sunlight or the heat from a fire falls on a surface, it exerts a

pressure on that surface tending to drive it back. The light from the lantern which was falling on the screen just now presses against the screen, though the whole pressure is exceedingly minute; the whole pressure of sunlight falling on the earth is something like 150,000 tons weight, a force which is insufficient to make the earth budge so much as one hair's breadth from its path. But on the small particles of a comet's tail its effect may be of importance, because although the force of pressure decreases with the size of the particle, it does not do so so rapidly as the volume or weight, so that the effect on the motion is up to a certain point greater the smaller the particle. In the case of a particle 1/20,000 in. in diameter, the light-pressure would just about balance gravitation; such a body would be neither attracted to nor repelled from the sun. For one whose diameter is 1/150,000 in., the repulsion of light-pressure would be twenty times gravitation. You will remember that Bredichin found three classes of tails, of which the one most powerfully repelled the repulsion was eighteen times gravitation. We have only to suppose that the particles are of this order of magnitude in order to account fully for his results. The existence of light pressure was deduced from theoretical considerations, but it does not depend on theory alone. The repulsion can be shown in the laboratory. Hull and Nichols actually tried to make an artificial comet, using the fine particles of lycopodium powder to show the repulsion of the tail. Unfortunately, although a repulsive force was shown, it was due mainly not to light pressure, but to another effect.

With a particle about 1/150,000 in. in diameter, the repulsion is twenty times the attraction of gravity. Can we proceed to still smaller particles and account for forces of 36, 90 units, or still higher? It appears not. The size mentioned is about the limit, and for small particles we find instead of increasing repulsion, less repulsion. Very minute particles offer practically no obstacle to the passage of light which, instead of pressing against them, bends freely round. I daresay by suitable assumptions, as to the density of the material, forces of 36 units might be accounted for, but the hypothesis of light-pressure seems hardly competent to account for the greater repulsive forces. It must not, however, be supposed that the theory of light-pressure is thus discredited; light pressure must act, and probably acts powerfully, on the minute particles which constitute a comet's tail, but a careful analysis of the strange motions and transformations taking place, has convinced many astronomers that other forces are at work modifying and in some cases increasing the repulsion. In this connection the evidence that the repulsion is by no means a constant force has obviously a most important bearing.

At first it is with an almost overwhelming sense of the complexity of the problem that we sit down before this mass of material striving to see through the twisting streamers and changing features to the few simple forces that govern it all. There are, however, a few signs of regularity in the photographs to which it seems most hopeful first to turn. I would therefore draw your attention to the envelopes. It is very difficult to reproduce these clearly on lantern slides, although they are plain enough on the original negatives. The envelopes are wreaths or veils thrown out towards the sun and flowing away on each side. They are not like the streamers from the nucleus, for they seem quite detached, forming an arch over the head. The mode of formation may be illustrated by a well known analogy. If you have a fountain consisting of a large number of jets of water in different directions, the limiting surface is a sort of dome in the form of a paraboloid, which, when seen sideways, exactly imitates the envelope of a comet. It is not merely a bounding surface beyond which none of the water is projected; the arch is thickened along this surface. When the water is turned on fuller, the arch rises; if it is turned off gradually it sinks, but if it is turned off suddenly the arch does not subside, but vanishes; the water of course subsides, but the thickening vanishes.

* A Discourse delivered before the Royal Institution, March 26, 1909.

It can hardly be doubted that the envelopes of a comet are formed in this way; the explosion, from which the envelope results, throws out matter with fairly uniform speed in all directions, this matter being under the influence of solar repulsion, just as in the analogous case the water was under gravitation. By studying them we can learn something of the explosions that produce them; further, in them we are concerned with the general mass of fine particles, so that the study of the rather exceptional knots and luminous patches is supplemented; and, finally, in them we have to deal with the repulsion of the particles, very shortly after they are projected, which is of special importance in the light of the recent evidence that the repulsion may cease to act.

The best defined and most regular envelopes on the Greenwich plates are those of October 27; the envelopes approach the parabolic form so closely as to confirm our hypothesis as to their formation, and to indicate that any disturbing forces are small. I give below some measures of two of the envelopes shown on that night on plates taken at various times. The first column shows the height of the arch deduced from measures made at the apex, that is to say by direct measurement; the second column from measures made of the direction of the envelope near the ends of the *latus rectum*, and therefore deduced indirectly. We have thus two independent determinations of the height.

The accompanying table show very characteristically the transitory nature of the envelopes and of the explosions. The large one, for instance, formed at about 8 h. 30 m. (it was hardly formed in the first photograph), and in the space of two hours subsided from its original height of 70,000 miles to 40,000 miles; that is the typical behaviour of envelopes; it indicates that the explosion is

Envelopes of Comet C, 1908 (Oct. 27).

(Distance of the vertex of the envelope from the nucleus of the comet).

Time.		Outer Envelope.		Inner envelope.	
		(1).	(2).	(1).	(2).
H.	M.	Miles.	Miles.	Miles.	Miles.
8	23	71,000	71,000	43,000	35,500
9	3	64,000	61,000	38,000	30,500
9	32	51,000	50,000	26,500	30,000
10	2	48,000	44,000	16,000	14,000
10	28	42,500	41,000	21,000	19,000

(1) Deduced from measurements made at the vertex.

(2) Deduced from measurements of the course of the envelope near the ends of the *latus rectum*.

strongest at first, and then dies down rapidly. But we can make another deduction: the envelope was beginning to form at 8 h. 23 m.; by 9 h. 3 m. the complete arch was visible. Now it can be shown theoretically that the formation of an envelope does not take place instantaneously along the entire arch; if, for example, the material forming the apex left the nucleus an hour previously, that forming the ends of the *latus rectum* left an hour and twenty-five minutes previously, and so on in proportion. Conversely, we can argue from the fact that the whole arch appeared in so short a time, and that the ends of the *latus rectum* begin to collapse very little, if at all, after the apex, that the time taken by the matter to travel from the nucleus to the apex must be very small. I dare not trust the figures in the Table so far as to calculate that time from them, but probably it will be a very safe outside limit if we say that that time is not more than two hours. A simple calculation shows that, for that to be the case, the solar repulsion acting on these particles must be at least 800 units—far larger than any repulsion calculated by Bredichin, Jaegermann, or others; the velocity of projection would need to be 70,000 miles per hour. These figures are far too startling for us to immediately accept them, though, of course, if it is admitted that the repulsion acts only for a short time, instead of continuously, it must be correspondingly more powerful during that time. We are at

the beginning not at the end of an investigation; but I am convinced that a great deal is to be learnt from the study of these envelopes. Unfortunately they are often very complicated. Sometimes two of them will intersect, or they may be all askew. That need not be considered surprising, for the simple parabolic form can only occur when the force of the explosion is equal in all directions.

Another feature sometimes possessing some degree of regularity is the waving of the streamers proceeding from the head. This is a feature which will certainly repay a much more careful examination than we have yet had time to give. The most immediately striking feature is that two or more of the streamers often run parallel to one another, their undulations exactly corresponding with the crest of one fitting over the crest of the other. As might be expected the undulations become larger, both in length and in amplitude, as we proceed outwards from the head. Professor Wolf has published some interesting data on this point. The thought suggests itself that the curves may be spiral curves produced by a rotation of the nucleus of the comet whilst it is discharging the streamers. The hypothesis is one which can probably be tested by careful measurement; meanwhile it appears to be more probable that the undulations, like so many other features, must be accounted for by changes, perhaps rhythmic changes, in the force of expulsion of the material.

Whatever may be the true cause of the phenomena of comets' tails, it is at least clear that the source of the power which forms them and which directs them is to be found in the sun. I am not sure that the exceptional activity of this comet is not due to the physical state of the sun at the time rather than to the constitution of the object itself. Certainly progress in explaining the phenomena is hampered by our partial ignorance of the electrical and physical conditions of the sun's surface. Therefore I cannot close this discourse without alluding to what is perhaps the greatest result of any that recent years have afforded to astronomy: Professor Hale's photographs of Solar Vortices and investigations of their magnetic fields. With the great Tower telescope in the clear atmosphere of Mount Wilson Observatory he obtained photographs of the remarkable structure, revealing to our eyes the gigantic whirlwinds raging over the solar surface above the sunspots. These photographs are taken with the light of one particular wave-length, the $H\alpha$ line of hydrogen. He has gone further and shown, I believe, to the satisfaction of physicists, that the light passing up through these vortices bears the sure marks of having passed through a strong magnetic field, whose lines run perpendicular to the solar surface, and that, according as the vortices rotate clockwise or counter-clockwise, the lines of magnetic force run from or into the sun. The chain of evidence seems to show that the field is produced by the rotation of negatively charged material in these vortices.

It would be hard to exaggerate the value of these latest revelations as to the condition of the sun, far though they are from satisfying our inquiries or enabling us to realise that power which over all the millions of miles convulses the comet and scatters its trailing debris to the remotest parts.

Platinum Trioxide.—Lothar Wöhler and F. Martin. —Freshly prepared white platinum dioxide hydrate, made from a strongly alkaline solution of dioxide salt, was dissolved in 2/N caustic potash, and the yellow solution was cooled and subjected to anodic oxidation. A deposit of silky-looking leaflets was rapidly formed upon the anode. This substance is an alkaline salt of platinum trioxide, apparently of formula $3PtO_3 \cdot K_2O$. The free oxide can be obtained by treatment with dilute acids. It is a very easily decomposed substance, readily giving up oxygen. Dilute acids, with the exception of 2/N hydrochloric acid, do not affect it. It is not reduced by hydrogen peroxide, but must be regarded as an anhydride of platinic acid.—*Berichte*, xlii., No. 13.

A NEW METHOD FOR MEASURING
THE ELECTROLYTIC DISSOCIATION OF WATER.

By C. S. HUDSON.

IN a recent article (*Journ. Am. Chem. Soc.*, 1907, xxix., 1571) it was shown that the measurements of the velocity-coefficient of the mutarotation of glucose in acid, alkaline, or neutral solutions are accurately expressed over the whole range by the formula $k = A + B(H^+) + C(OH^-)$, where k is the velocity-coefficient, A , B , and C are constants, and H^+ and OH^- are the concentrations of hydrogen- and hydroxyl-ions, respectively, in the solutions. For neutral solutions or pure water let the velocity-coefficient be written k_w , and the hydrogen-ion concentration which is equal for this case

value was found. Those values which were later shown to be erroneous are enclosed in brackets.

The accuracy of the method which is here described for measuring the electrolytic dissociation of water depends primarily on the accuracy with which the difference $k_w - A$ can be measured. For glucose this difference is only 10 per cent of the separate quantities, and consequently the accuracy of the method is not great, probably about 20 per cent, but from recent measurements which the writer (*Journ. Am. Chem. Soc.*, 1908, xxx., 1578) has made on the rate of mutarotation of the related sugar fructose in pure water and acid solutions, it appears that the above difference for this sugar is far greater than for glucose, being over 40 per cent of the separate quantities. Measurements on fructose will, therefore, in all probability give

The Hydrogen-ion Concentration of Pure Water near 25° C.

H ⁺ =OH ⁻ (grm.-molecules per litre × 10 ⁷).	Tempera- ture. °C.	Investigator.	Date.	Method of determination.
[6.0] [9.0] 1.1	25	Ostwald (<i>Zeit. Phys. Chem.</i> , 1893, xi., 521)	1893	Electrical conductance of pure water. Acid-alkali hydrogen cell.
	25	Arrhenius (<i>Ibid.</i> , 1893, xi., 823; see also Shields, <i>Ibid.</i> , 1893, xii., 184)	1893	Hydrolysis of sodium acetate by ester saponification.
[0.1] [6.0]	11	Wijs (<i>Ibid.</i> , 1893, xi., 492)	1893	Aqueous saponification of methyl acetate.
	25	Bredig (<i>Ibid.</i> , 1893, xi., 829; see Arrhenius, <i>Ibid.</i> , 1890, v., 19; and Walker, <i>Ibid.</i> , 1889, iv., 334)	1893	Hydrolysis of aniline acetate from conductivity measurements.
	25	Wijs (<i>Ibid.</i> , 1893, xii., 514)	1893	Aqueous saponification of methyl acetate.
1.2 0.8	18	Nernst (<i>Ibid.</i> , 1894, xiv., 155; a new theory of this method is there given by Nernst)	1894	Acid-alkali hydrogen cell.
1.05	25	Kohlrausch and Heydweiller (<i>Ibid.</i> , 1894, xiv., 330)	1894	Electrical conductance of pure water.
1.2 0.91	25	Löwenherz (<i>Ibid.</i> , 1896, xx., 293). A. A. Noyes and Kanolt (Carnegie Institution of Washington, 1907, Publication 63, p. 297) . .	1896	Acid-alkali hydrogen cell.
			1907	Hydrolysis of ammonium diketotetrahydrothiazole from conductivity measurements.
1.0	25	Hudson	1909	Catalysis of the mutarotation of glucose by acids and alkalis.

to that of the hydroxyl-ion be written H_w ; the above formula then takes the form, for pure water or neutral solutions, $k_w = A + (B + C)H_w$. Solving this expression gives $H_w = \frac{(k_w - A)}{(B + C)}$. This relation gives a new method for

measuring the hydrogen-ion concentration, or, in other words, the electrolytic dissociation of water, for the four quantities on the right-hand side of the equation can be determined experimentally by measuring the rate of mutarotation of glucose in ordinary distilled water and in acid and alkaline solutions. The first formula above is based on measurements of the rate of mutarotation of glucose in in alkaline solutions by Osaka (*Zeit. Phys. Chem.*, 1900, xxxv., 702), and similar ones in acid solutions by the writer (*loc. cit.*), and has the form, as was shown in the previous article, $k = 0.0096 + 0.258(H^+) + 9750(OH^-)$, k being expressed in minutes and decimal logarithms, H^+ and OH^- in grm.-molecules per litre, and the temperature being 25° C. The constants for glucose at 25° are therefore $A = 0.0096$, $B = 0.258$, and $C = 9750$. The velocity-coefficient for pure water was found at the same time to be $k_w = 0.0106$, which agrees closely with the value which Osaka found, 0.0104. The substitution of these constants in the formula preceding gives $H_w = 1.0(10)^{-7}$, a value which is in close agreement with those that have been found in the past from measurements that are based on entirely different facts and principles. In the accompanying table is recorded a list of the values for the hydrogen-ion concentration of pure water which have been found by various investigators, together with a statement of the method by which the

with closer accuracy the electrolytic dissociation of water.—*Circular No. 45*, United States Department of Agriculture, Bureau of Chemistry.

A REVISION OF THE ATOMIC WEIGHT OF
CHROMIUM.*

SECOND PAPER.—THE ANALYSIS OF SILVER DICHROMATE.

By GREGORY PAUL BAXTER
and
RICHARD HENRY JESSE, Jun.

IN a former paper (*Journ. Am. Chem. Soc.*, xxxi., 529; *CHEMICAL NEWS*, c., 180 *et seq.*) is described a successful attempt to prepare pure silver chromate and to determine its silver content, with the object of throwing light upon the atomic weight of chromium, the value found in this way, 52.01, being about one-tenth of a unit lower than the one in common use. The preparation and analysis of silver dichromate was next investigated. Since the proportion of chromium in the dichromate is 50 per cent larger than in the chromate, the effect of experimental uncertainty upon the final result is correspondingly reduced.

Silver dichromate possesses another great advantage over silver chromate for exact work in that it may be readily crystallised from nitric acid solutions, and thus be freed

* Contributions from the Chemical Laboratory of Harvard College. From the *Journal of the American Chemical Society*, xxxi., No. 5.

from impurities included or occluded during precipitation, with the exception of nitric acid and moisture. For, the silver and chromium being present in equivalent proportions during the crystallisation, the inclusion of mother-liquor could do no harm. If the concentration of the nitric acid is sufficiently high, there is no possibility of the separation of silver chromate as such during this crystallisation, since Sherrill (*Journ. Am. Chem. Soc.*, 1907, xxix., 1641) has shown that silver chromate changes rapidly into silver dichromate under nitric acid solutions more concentrated than 0.075 normal. This is primarily due to the low value of the dissociation constant of the second hydrogen of chromic acid, which has been found by Sherrill to be 6×10^{-7} , the solubility product of silver chromate being 9×10^{-12} , and that of silver dichromate being 2×10^{-7} . Sherrill has also investigated the part which the hydrochromate ion plays in the equilibrium relations of chromates and dichromates in solution, and has found the following equation to hold:— $(\text{Cr}_2\text{O}_7^{2-})/(\text{HCrO}_4^-)^2 = 75$.

Although obviously the concentration of the hydrochromate ion in dichromate solutions (in a 0.1 molar solution of potassium dichromate 15 per cent of the salt existing as hydrochromate) is always considerable, the precipitation of the solid phase AgHCrO_4 seems not to be possible. Sherrill was not able to find any indication of the presence of this salt in the precipitate formed by adding silver nitrate to chromic acid in nitric acid solution. Furthermore, since the water content of our material was carefully investigated, the presence of hydrochromate in traces could do no harm, for the latter substance upon sufficient heating would yield dichromate and water according to the following equation:— $2\text{AgHCrO}_4 = \text{Ag}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{O}$.

Although the presence of polychromates other than the dichromate seemed improbable, their absence from our material was shown by crystallising silver dichromate from nitric acid of different concentrations. Since this variation was without effect, it may be reasonably supposed that more highly acid salts than the dichromates were neither precipitated as solid phases nor occluded.

Purification of Materials.

Only slight changes were made in the methods of purifying the materials used in the various preparations of silver dichromate, and in the analyses from those described in the former paper.

Nitric Acid.—Nitric acid was freed from chlorine by several distillations through a platinum condenser.

Hydrochloric Acid.—This acid also after dilution was purified by distillation with a quartz condenser.

Hydrobromic Acid.—Hydrobromic acid was prepared from bromine which has been twice distilled from solution in potassium bromide, the bromide in the second distillation being essentially free from chlorine. The hydrobromic acid was synthesised by passing carefully cleansed hydrogen (made from the lead-sodium alloy "hydrone" and water) through the bromine at about 40°, and then over hot platinised asbestos, the acid being collected in pure water. Iodine was eliminated from the acid by boiling with free bromine several times. Finally, it was re-distilled through a quartz condenser three times with rejection of the extreme fractions. The acid diluted to normal concentration, was kept in a well-protected glass bottle.

Silver Nitrate.—Silver nitrate was prepared from silver which had been precipitated once as chloride, and then reduced with invert sugar. The nitric acid solution of the fused mass was evaporated to crystallisation, and the salt was then three times more crystallised from nitric acid solutions, the crystals being drained centrifugally in a centrifugal machine, employing platinum Gooch crucibles as baskets (*Journ. Am. Chem. Soc.*, 1908, xxx., 286). Heating was carried out over electric stoves in order to avoid contamination by the combustion products of illuminating gas, both in this and in all other preparations in this research.

Potassium Dichromate.—The best commercial material

was crystallised four times, once from aqueous solution in Jena glass, and three times in platinum vessels.

Chromic Acid.—This substance was three times re-crystallised in platinum vessels as described in the former paper.

Silver Dichromate.—Silver dichromate was prepared by combining either potassium dichromate or chromic acid with silver nitrate in nitric acid solution in platinum vessels. Precipitation was carried out in fairly concentrated solution, since in the subsequent crystallisation of the silver salt from nitric acid solution any included substance was sure to be eliminated. Although the inclusion of nitric acid during the crystallisation was to be feared, and was actually found to have taken place, a method was devised for the determination of this nitric acid, together with the moisture retained by the solid.

Sample I.—Silver nitrate and potassium dichromate were dissolved in equivalent proportions in 3 normal nitric acid, the concentration of each salt being 0.7 normal. The cold silver nitrate solution was added very slowly, with constant vigorous stirring, to the dichromate solution. After the precipitate had been allowed to settle, the mother-liquor was decanted, and the precipitate was centrifugally drained, and rinsed in the centrifugal machine with 3 normal nitric acid.

The salt was then five times re-crystallised from solution in 3 normal nitric acid with centrifugal drainage after each crystallisation. Owing to the small solubility of silver dichromate in nitric acid solutions the following scheme of crystallisation was adopted:—The dichromate was heated with the nitric acid solution upon the electric stove until the acid was saturated with silver dichromate. Then the hot solution was decanted into a dish through a platinum Gooch crucible without a mat of any sort but with small holes, in order to remove particles of silver dichromate either suspended in the solution or floating on the surface. These particles were always of considerable size, so that the resulting solution was clear. After the saturated solution had cooled and had deposited the greater part of its charge of salt, the mother-liquor was continuously used to dissolve fresh portions of the salt. About 1 litre of acid was used for the crystallisation of about 50 grms. of dichromate. Although by this method the impurities in the original salt accumulate in the mother-liquor, on account of the relatively large volume of the mother-liquor, there was little danger of these impurities being carried into the second crop of crystals. It was shown, for instance, that the mother-liquor from the third crystallisation was free from potassium. This mother-liquor was evaporated to small bulk, neutralised with ammonia, and reduced and precipitated with hydrogen sulphide. The filtrate after evaporation and expulsion of the ammonium salts gave no spectroscopic flame test for potassium.

The silver dichromate was not allowed to come in contact with water or any solution except the 3 normal nitric acid solution.

All of the above operations were carried out in platinum vessels.

Sample II.—This sample was made exactly as in the case of Sample I., except that chromic acid was employed instead of potassium dichromate, and that both precipitation and crystallisation took place from 0.8 normal nitric acid. The silver dichromate was crystallised five times.

Sample III.—The most dilute nitric acid which was used in the preparation of the silver dichromate was about 0.16 normal, solutions of this concentration being employed in the precipitation and crystallisation of Sample III. This sample was made from chromic acid and silver nitrate, and was six times crystallised from 0.16 normal nitric acid.

The chief difference in the purification of the three specimens, aside from the concentrations of acid used in their preparation, lies in the fact that Sample I. was prepared from re-crystallised potassium dichromate, and Samples II. and III. from chromic acid. All three samples were crystallised many times as silver dichromate.

After the final drainage in the centrifugal apparatus, the crystals were dried in an electric oven at 150° for several hours. Then they were powdered gently in an agate mortar and kept in platinum vessels.

The Determination of Silver in Silver Dichromate.—In preparing the silver dichromate for analysis, the complete elimination of moisture by fusion of the salt was impossible, owing to the ease with which silver dichromate decomposes. Even at the comparatively low temperature of the melting-point of the dichromate, about 400° , oxygen is given off rapidly, while at temperatures considerably below this point, 300° , and to a very slight extent at 250° , there seemed to be evidence of decomposition, since salt heated to these temperatures did not give an absolutely clear solution in dilute nitric acid. In order to be on the safe side, the drying of the salt took place at 200° .

The heating of the dichromate was affected much as described in the former paper in the case of silver chromate. The salt, contained in a weighed platinum boat, was heated in a current of pure dry air in a hard glass tube for four hours at 200° , the air being purified and dried by passing over hot copper oxide, solid potassium hydroxide, concentrated sulphuric acid containing dichromate, and re-sublimed phosphorus pentoxide successively. An oven composed of solid aluminium blocks was used, by means of which the temperature could be maintained constant within 2° (Baxter and Tilley, *Journ. Am. Chem. Soc.*, 1909, *xxi.*, 206).

After the boat had been allowed to cool in the tube, it was transferred to the weighing bottle by means of a "bottling apparatus," and was re-weighed (Richards and Parker, *Proc. Am. Acad.*, 1896, *xxxii.*, 59). Then the dichromate was transferred to a flask, and was dissolved in hot 0.8 normal nitric acid. The solution, which was always perfectly clear, was quantitatively transferred to a 3-litre glass-stoppered precipitating flask, and at a dilution of about 1 litre was reduced by the addition of a very slight excess of sulphur dioxide. When the solution was cold, a slight excess of hydrobromic acid was diluted to about 800 cc., and then was slowly added to the silver solution with continual agitation. The flask was stoppered and vigorously shaken. After twenty-four hours' standing, the flask was again shaken, and then was allowed to stand two days or more, until the supernatant solution was clear.

Next, the silver bromide was collected upon a weighed Gooch crucible, dried, and weighed. The asbestos mechanically detached from the Gooch crucible was collected upon a small filter-paper. In order to avoid any danger from adsorption of chromic salts by the filter-paper, at the end of the filtration the paper was rinsed with hot dilute hydrobromic acid. The correction for asbestos could have been avoided if it had been possible to employ a Gooch-Munroe-Neubauer crucible with a mat of platinum sponge. It has already been shown, however, in the former paper (*loc. cit.*), that such crucibles lose appreciably in weight when exposed to the action even of dilute *aqua regia* of the mother-liquors of these analyses. The moisture retained by the silver bromide was found by fusing the dried salt in a porcelain crucible, the loss in weight on fusion being determined. The fused silver bromide was always light yellow, and gave every indication of purity.

As in the former research, a small quantity of silver bromide dissolved in the filtrate and wash-waters was found by evaporating the combined filtrate and wash-waters until nearly all the excess of acid had been expelled, and then, after slight dilution, precipitating the silver as sulphide. The sulphide was collected on a small paper, the ash of which, after ignition, was treated with nitric acid. The amount of silver thus obtained was found by comparison in a nephelometer of precipitates of silver bromide produced in this solution, and in very dilute standard solutions of silver.

In Analysis 9, the silver was precipitated as silver chloride, the only other difference in the procedure being that the precipitate was washed with dilute hydrochloric acid instead of pure water.

The Determination of Moisture and Nitric Acid in Silver Dichromate.—Silver dichromate which has been crystallised from nitric acid, after being dried at 200° , contains traces of both nitric acid and water. Both of these substances can be expelled from the salt by fusion, although slight decomposition of the salt takes place simultaneously. Since the only readily volatile substance which can be formed by the decomposition of the salt is oxygen gas, the problem of the determination of the moisture and nitric acid consisted in that of absorbing in a quantitative fashion the water, nitric acid, and nitric peroxide formed by decomposition of the nitric acid. This was effected by passing the current of air containing the moisture and nitrogen compounds through two weighed U-tubes, one containing a concentrated solution of potassium hydroxide and solid potassium hydroxide, and the other re-sublimed phosphorus pentoxide. The air current passed first through the potassium hydroxide tube in order that moisture vaporised from the hydroxide might be retained by the pentoxide tube. That the absorption of oxides of nitrogen was complete was shown by the fact that no test for nitric acid could be obtained beyond the phosphorus pentoxide tube either with moist litmus-paper or with diphenylamine.

Since the three samples of silver dichromate were crystallised from nitric acid of different concentrations, it was necessary to make separate determinations of the moisture and nitric acid content with each sample. Extreme purity of material was unnecessary, and, as rather large quantities of salt were desired, three samples were prepared from ordinary silver nitrate and potassium dichromate, and then were crystallised from nitric acid of the concentrations 3 normal, 0.8 normal, and 0.16 normal, respectively, glass vessels being employed throughout.

Weighed portions of the silver dichromate were heated for four hours at 200° in a current of pure dry air exactly as in preparing the salt for the silver analyses. Then the weighed potassium hydroxide and phosphorus pentoxide tubes were attached to the hard glass tube, with a protection tube containing phosphorus pentoxide at the end. The silver dichromate was gradually heated to complete fusion, and the air current was allowed to pass through the system for one-half hour in order to make certain that all the vapours expelled from the dichromate were carried into the absorbing tubes. The absorption tubes were then re-weighed.

Before the tubes were weighed they were carefully wiped with a clean damp cloth, and were allowed to stand near the balance case for one hour. The tubes were provided with ground glass stopcocks lubricated with Ramsay desiccator grease. During the weighing, one stopcock in each tube was open to equalise the air pressure within and without the tubes. In order to lessen the error in weighing, as well as to save time and labour, the tubes were not weighed separately, but together as one system. Counterpoise tubes of the same shape and size were always employed. Blank determinations showed that the air current and manipulation of the tubes caused an increase in weight of 0.00010 grm. in one-half hour. This quantity is applied as a correction in every case.

In place of a platinum boat a superficially oxidised copper boat was used in these experiments. At the low temperature of fusion of silver dichromate there is little danger of decomposition of nitric acid or oxides of nitrogen by the oxidised copper. It is to be noted that if the nitric acid is decomposed during the experiment according to the following equation — $2\text{HNO}_3 = \text{H}_2\text{O} + 2\text{NO}_2 + \text{O}$, and is absorbed by the potassium hydroxide as NO_2 , there is a slight loss of oxygen. The proportion of nitric acid present being very small, however, this error could have no appreciable effect on the results.

It is somewhat surprising that Samples I. and II. contain the same proportion of volatile matter. This agrees with the result of the silver determinations, however, the samples proving to be otherwise very similar. As is to be expected,

Sample.	Weight of $\text{Ag}_2\text{Cr}_2\text{O}_7$.	Gain in weight of absorption tubes.	Gain. Weight of $\text{Ag}_2\text{Cr}_2\text{O}_7$.
I.	22.52	0.00448	0.000194
I.	20.74	0.00378	0.000177
I.	12.25	0.00235	0.000184
Average			0.000186
II.	13.13	0.00309	0.000235
II.	15.91	0.00317	0.000193
II.	21.35	0.00391	0.000178
II.	19.60	0.00373	0.000185
Average, rejecting the first determination			0.000186
III.	20.89	0.00353	0.000164
III.	19.94	0.00348	0.000169
Average			0.000167

Sample III. contains less impurity than either of the other two.

The negative corrections as found above are applied to all the final weights of silver dichromate given in the table of analyses.

(To be continued).

SOME FORMS OF FOOD ADULTERATION AND SIMPLE METHODS FOR THEIR DETECTION.*

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and
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(Continued from p. 203).

FORMS OF ADULTERATION OF SPECIFIC FOODS.

THE samples submitted to analysis were not usually representative samples. The inspectors in the various States are trained men, and are always instructed to select especially those samples which they have reason to believe are likely to be adulterated. Brands of food which they know from previous experience are pure are, therefore, not commonly taken by these inspectors, and products whose purity for any reason they are inclined to suspect are sampled. In the report of each laboratory, therefore, the percentage of adulterated samples is stated, not in terms of the average foods of the State, but in terms of the foods which experienced inspectors have regarded with suspicion.

Baking Powders and Baking Chemicals.

Baking powders consist of a mixture of bicarbonate of soda with some acid ingredient. When the powders are moistened, these two substances unite and liberate carbon dioxide gas. To prevent the two substances mentioned above uniting prematurely while the baking powder is still in the package, owing to moisture in the atmosphere, starch is usually employed as a filler. Some brands are claimed by the manufacturers to contain no filler, but to consist exclusively of sodium bicarbonate and the acid ingredient employed.

These substances are used as the acid ingredient of baking powder—cream of tartar, alum (basic aluminium sulphate), and acid phosphate. In some powders a mixture of alum and acid phosphate is employed. Sometimes the amount of filler employed is excessive, and sometimes foreign mineral matter is present. Perhaps the most objectionable form of adulteration of baking powder that has occurred in recent years was the use of a considerable percentage of ground soapstone. The particles of stone

were sharp-cornered and decidedly inappropriate for use in the preparation of foods.

The cream of tartar on the market is frequently adulterated with other acid substances, such as alum and acid calcium phosphate. These materials are of a more acid nature than cream of tartar, and permit of the addition of a considerable percentage of inert material which is often employed.

Beverages.

Alcoholic.—Wine is sometimes prepared artificially by the fermentation of glucose with the addition of resins, or some fruit juice, and artificially coloured. Such products, however, are probably not sold as a beverage to any extent, and do not form an important part of our commerce. The cheaper grades of wine are sometimes coloured artificially and chemically preserved.

Carbonated wines, prepared by means of dissolving in them carbon dioxide gas under pressure, are sometimes sold as champagne. On the whole, the fraudulent practice most frequently employed with wine is misbranding with regard to its variety and place of manufacture.

Beer is frequently preserved chemically. In the case of whisky and brandy artificial products are often sold under labels which represent them to be natural products. So-called essences are made on the manufacturing scale and sold commercially for the preparation of beverages intended to represent the various classes of distilled liquors. To these products a small amount of soap is sometimes added to produce a "bead."

Non-alcoholic.—Non-alcoholic beverages, such as ginger ale and the various fruit syrups, are frequently preserved with salicylic acid and benzoic acid, and coloured with coal-tar derivatives. These products may be detected as described later on. Syrups for soda-water fountains are sometimes altogether artificial and are commonly preserved, coloured, and often flavoured artificially.

Canned Vegetables.

Canned vegetables constitute a class of products relatively free from adulteration by means of foreign substances. Imported canned peas are commonly coloured with copper sulphate. Owing to the enforcement of the imported food law by the Bureau of Chemistry, the presence of copper is now almost universally stated on the labels of these goods. Peas and beans grown and canned in America are rarely coloured.

One of the most frequent frauds in this class of products is the preparation of goods which have reached a relatively mature state, and the selling of such products as first grade. Mature peas, for instance, are sometimes soaked for the purpose of softening them, canned, and sold as peas of first quality. Again, peas that are not thoroughly ripe, but so nearly mature as to be relatively hard and white, are sometimes canned as a high grade article.

At the period at which sugar corn is canned the sugar disappears very rapidly after picking, and it is customary to add some sugar at the time of canning. During recent years many canning establishments replaced sugar with saccharin, an artificial sweetening material derived from coal-tar. A few years ago it was customary to bleach corn for canning by means of sulphites, but this practice has been almost entirely discontinued.

Tomatoes are sometimes coloured artificially in order to add to the price of an inferior article.

Cereal Products.

Breakfast Foods.—During the last few years the number of breakfast foods on the market has been enormously increased, and very many of them are extensively advertised by means of greatly exaggerated statements regarding their nutritive value. Some of these products are simply ground with no other preparation than the removal of the hulls, &c. Others are partially cooked, and still others are "predigested" by means of special treatment.

There appears to be some doubt as to the amount of

* *Bulletin* No. 100, Bureau of Chemistry, U.S. Department of Agriculture.

advantage derived from the treatment to which the partially cooked and pre-digested foods are subjected. All breakfast foods when thoroughly cooked seem to be equally as digestible as the products placed on the market in a more advanced state of preparation.

The rumours which have been circulated from time to time that arsenic and other poisonous substances are used in breakfast foods have been entirely without foundation. There is no doubt of the wholesomeness of these foods. At the same time the exaggerated claims made by the manufacturers regarding their superior nutritive qualities are to be deplored.

Flour.—There is an impression in some quarters, unfortunately, that flour is adulterated with ground gypsum or other mineral matter. It is also believed by many that alum is used for the purpose of whitening bread. It may be said, however, that these forms of adulteration are not practised in this country.

Some years ago an effort was made to place on the market a ground stone for the purpose of adulterating flour. This product was extensively advertised by means of circular letters addressed to millers. As far as we have been able to ascertain, however, the product was never used. At one time during recent years the use of Indian corn flour for the adulteration of wheat flour became somewhat prevalent. This practice was entirely stopped by the enforcement of the Federal law relating to mixed flour. At the present time there is probably no product on our market more free from adulteration than wheat flour.

Some adulteration is practised in special kinds of flour. For instance, much of the so-called gluten flour on the market is not at all what it purports to be. Frequently untreated wheat flour is sold for gluten flour. Buckwheat flour and other special articles of that nature are also frequently adulterated with cheaper cereal products.

Cocoa and Chocolate.

In the preparation of cocoa and chocolate, cocoa beans are roasted, freed from shells, and ground. The resulting product is known as cocoa mass. It contains about 50 per cent of fat (cocoa butter), and is sometimes melted into cakes without any further addition, and sold as plain chocolate or bitter chocolate.

For the preparation of sweetened chocolate, cane sugar is added to the cocoa mass and ground at a temperature sufficient to melt the fat. Milk chocolate is prepared by mixing with the cocoa mass dry milk powder (obtained by the evaporation of whole milk) and sugar.

Cocoa is obtained by pressing the cocoa mass while still sufficiently warm to melt the fat so that a portion of it is removed. The fat is melted into cakes and sold as cocoa butter, while the pressed cakes of cocoa from which a portion of the fat has been extracted are ground up in the preparation of breakfast cocoa.

For the purpose of cheapening cocoa and chocolate, starches of various kinds are ground in with the cocoa mass at the time of the introduction of the sugar or with the cocoa after the expression of the fat. (A list of the various starches that have been reported from different sources is given in this *Bulletin*). With a few exceptions the adulterants reported in this class of products are not injurious to health except in so far as they reduce the nutritive value of the product. At the same time such products as iron oxide, sawdust, sand, and woody shells can not be regarded as wholesome and should not be added to foods.

Coffee and Tea.

Owing to the enforcement of the Federal tea law by inspectors stationed at all ports of entry, it is believed that no adulterated tea comes into this country, and it is probably true that the adulteration of this product is not practised after entry. Formerly it was believed that many other leaves were used as substitutes or adulterants for tea, and a sample may be readily examined for such adulterants by thoroughly wetting and unrolling the leaves and noting their shape.

With regard to coffee, however, while it is believed that only the pure product is brought into the country, its adulteration after reaching our shores is not uncommon. The attempts that have been made to imitate the coffee bean have not been commercially successful, but the ground coffees sold in the market are frequently adulterated. For this purpose chicory was usually employed, but has since been largely replaced by articles of lower value—ground peas, wheat, beans, barley, &c., now being commonly used. The principal offence in the coffee trade is misbranding as to country of origin. The sale of Brazilian coffee, for example, as Java or Mocha is unfortunately very common.

The artificially moulded coffee berries, referred to above, are not on the market, as far as is known, but may be readily distinguished by cutting a cross section of the bean and examining its structure. That of the artificial bean is of a compact, solid, uniform nature, whereas the true coffee has a characteristic structure that can not be imitated. If pure coffee is desired, therefore, the most practical plan is to buy it unground.

Condimental Sauces.

The term "condimental sauces" as here used is intended to apply to catsups, pickles, and miscellaneous sauces. It is not intended to include vinegar or spices, which are considered under other captions.

Catsups are very commonly coloured and preserved. In the home a single bottle of catsup may be kept open for a considerable time, and a demand has been found for preserved goods in order that the bottle may be kept without deterioration of the contents for some time after it is opened. Again, some manufacturers buy the greater part of the tomatoes used in making catsup within a very short period in the summer. They then prepare the pulp and store it in barrels, preserved with benzoic or salicylic acid to prevent its spoiling. Owing to the demand for catsups free from preservatives, however, some firms are now preparing their goods in small bottles sterilised by heat. These are found to keep perfectly well before opening, but of course must be used within a reasonable time after they are opened, and be kept in a cool place. An additional expense attends the preparation of goods in this manner, as it is necessary to preserve the pulp by means of sterilisation by heat until such time as it is desirable to prepare the catsup.

Pickles are sometimes coloured with copper, as in the case of imported peas and beans.

Dairy Products.

Butter.—The sale of oleomargarine as butter was formerly very common, but the enforcement of the internal-revenue laws relative to that subject by the Treasury Department, and of the State laws (U.S. Dept. of Agr., Bureau of Chemistry, *Bull.* 69 Revised, Parts I.—VIII., Foods and Food Control), have greatly lessened this species of fraud, although violations of these laws still occur with considerable frequency.

It is now the custom to treat much of the rancid butter on the market in such a way as to remove the rancidity in the preparation of what is known as "process" or "renovated butter." In the early days of the manufacture of this article it was ordinarily sold as fresh butter. At the present time, however, this product is required to be marked on the wrapper with the words "Renovated Butter," and violations of the law requiring this are relatively infrequent. This law is enforced by the Bureau of Animal Industry of the Department of Agriculture in collaboration with the Treasury Department (U.S. Dept. of Agr., Bureau of Chemistry, *Bull.* 69 Revised, Part I., p. 28). The chemical analyses necessary in the enforcement of the law are made in the Bureau of Chemistry.

Butter is sometimes preserved with boric acid, and glucose has sometimes been found as an adulterant. The colouring of butter is usual, and is permitted by the laws

of all the States. The principles governing the legislation regarding colouring matter of foods in general have not been ordinarily applied to the colouring of butter. The present tendency, however, seems to be to prepare butter with a lighter tint, and a more natural-looking article can now be found in the market than formerly.

Cheese.—One of the most frequent methods of adulterating cheese is to prepare it from milk which has been skimmed and to which some other form of fat has been added for the purpose of replacing the fat of the cream removed. Both lard and cotton-seed oil have been used for this purpose. Cheese which has such an addition of foreign fat is known as "filled cheese." Such a product well illustrates a form of adulteration which, although it may not be at all unwholesome, is fraudulent, and if sold as full cream cheese constitutes a form of misbranding. Such a sale is unfair to the buyer, aside from the question of price. If the cheese is desired for melting, as in making a Welsh rarebit, or for other use in cooking, the foreign fat or oil of the filled cheese will separate much more readily than from a genuine cheese, leaving a gummy mass, instead of melting smoothly as a full cream cheese will do.

Cream.—Cream is frequently preserved artificially. This is illegal in most of the States, but some which prohibit artificial preservatives in milk permit them in cream. How this position is justified does not appear. During recent years preparations known as "thickeners" have been sold to permit dealers to sophisticate their wares. These thickeners ordinarily consist of gelatin, and sometimes contain boric acid for the purpose of preserving the cream.

Since in the use of cream the dietetic value of fat is taken into consideration, and especially since it is frequently employed in the preparation of modified milk for the use of infants, the sale of a product in which the fat has been largely replaced by gelatin should be condemned in strong terms.

Milk.—The most serious problem connected with food control is the regulation of the milk supply. A considerable portion of the milk consumed is employed as food for infants and invalids. In such cases it frequently forms the entire food consumed by an individual. For that reason, and because of the susceptibility of infants and invalids to interfering substances, it is imperative that the quality of the milk supply be carefully guarded.

The addition of preservatives to milk is particularly to be condemned, partly because of the influences of the preservative itself on the health of infants and invalids by whom the milk may be used as a food, and partly because of the less cleanly methods that may be employed in the preservation of milk when preservatives are used, and of the increased danger in the consumption of such milk.

The most common adulteration practised with milk is the addition of water or the removal of cream. The management of the dairy and the care of the milk from the time it is received from the cow until it is delivered to the consumer are attended by great difficulties. If the milk is to be kept without chemical preservation, absolute cleanliness and prompt, intelligent care are imperative. This is true at all times, and especially in the summer. The milk must be cooled immediately and kept cool until its delivery to the consumer, and then delivery must not be delayed too long. Even after the milk is left at the door of the consumer considerable annoyance is caused by many who do not take their milk promptly and place it in the refrigerator. It is frequently allowed to stand at the door for a considerable time, and then many cases of spoiling for which the consumer is responsible are attributed by him to the dairymen.

In order to avoid these inconveniences the use of preservatives with milk is frequently practised wherever the enforcement of the food laws is not rigid. In this connection especially the use of commercial preservatives represented to be in conformity with the food laws is of interest.

Edible Fats and Oils.

The substitution for high-priced fats and oils of products of the same class but of lower commercial value is very common. Of special interest in this connection is the sale of cotton-seed oil, pea-nut oil, and sesame oil for olive oil. Until 1903, when the enforcement of the imported food law was begun by the Bureau of Chemistry, much of the olive oil imported into the country was adulterated by means of the oils mentioned. This practice has now been practically stopped. At the same time there is no Federal legislation which prevents the importation of these oils separately and their mixture in this country, and to a certain extent this is done. The relative dietetic properties of the various oils have not been carefully studied, and this form of adulteration is therefore to be condemned, not because of its bearing on dietetics, but because of its fraudulent nature.

Lard is often mixed with other fats, such as tallow and cotton-seed oil. Such mixtures are legitimate when sold as compound lard, but that their sale as lard has been practised to a considerable extent is shown by a table in this *Bulletin*.

The lard sold in tropical and subtropical countries is of a different nature from that sold in cooler places. It is stated by manufacturers that natural lard is too soft a product for marketing in warm weather, and that it can be greatly improved in this respect by the addition of a fat of a firmer nature. For this purpose stearin, that portion of the ordinary fats which melts at the highest temperature, is sometimes employed. Stearin is prepared by heating fat such as beef suet or lard to a temperature sufficient to melt a portion of the product, but insufficient to melt stearin, and then filtering by means of pressure through bags prepared for that purpose. The stearin which is not melted is frequently added to the commercial lard for the purpose of making it more firm than it otherwise would be, as stated above. Less stearin is necessary for this purpose in winter than in summer, and less in cool climates than in hot. A considerable portion is employed for lard used in tropical countries. Beef stearin is sometimes employed for this purpose, although lard stearin is frequently used, especially in the preparation of lard intended for States forbidding the addition of beef fat to lard.

Flavouring Extracts.

The class of products comprising flavouring extracts is very frequently adulterated. Artificial extracts are commonly sold instead of those prepared from natural sources, and cheaper products than those supposed to be used are often employed. For instance, tonka beans are used instead of vanilla beans in the preparation of supposed vanilla extract, and artificial vanillin, a coal-tar derivative, is very commonly employed in the preparation of the cheapest grade of vanilla extract.

Lemon extract, supposed to be manufactured by dissolving lemon oil in alcohol, may be made from lemon grass. Lemon oil is sometimes treated by distillation with steam, and the non-volatile portions employed in the preparation of lemon extracts, while the volatile portions containing the terpenes (an essential characteristic of lemon oil) of the oil are sold as lemon oil. Practically the same forms of adulteration are practised with other classes of flavouring extracts.

Lemon oil is almost insoluble in water, and a fairly strong alcohol is required to obtain it in the strength desired for flavouring purposes. Many manufacturers have unintentionally violated the law by attempting to dissolve lemon oil in alcohol that is not sufficiently strong. They frequently believe that their extract is up to the standard when as a matter of fact only a small portion of the oil they employ is dissolved in the weak alcohol, and the remainder is unintentionally discarded. A lemon extract having but a small amount of alcohol must necessarily have a low percentage of oil of lemon.

(To be continued),

NOTICES OF BOOKS.

The New Physics : Sound. By JOSEPH BATTELL.
Middlebury, Vermont: American Publishing Company.
London: Arthur F. Bird. 1909.

THE author of this book endeavours to convince his readers that sound is corpuscular, defining it as particles of electrical matter produced by shock. He has two ways of refuting, apparently to his own satisfaction, arguments in favour of the undulatory theory; the first and simplest is to denounce them as "inconceivably stupid," and so leave it. The second is to refuse to accept any experimental facts which cannot well be explained by his theory, and this however well attested or easily reproduced the experiments may be. He scorns his opponents for being satisfied with mere hypotheses, but at the same time shows that he is capable of forming ingenious hypotheses himself. For instance, he can offer a suggestion to explain away interference, and declares that if it be really true that sound is not transmitted in a vacuum, the correct conclusion to be drawn is that sound is composed in part at least of material made from the air. He brings forward no facts which are not perfectly satisfactorily explained by the undulatory theory, and the text suggests strongly that he is not familiar at any rate with modern treatises on physics. Still it requires some temerity to combat universally accepted and well established views, and no doubt the author feels that unless his language is vigorous and his wording unequivocal his theory may be passed over without notice.

Deuxième Congrès International pour la Répression des Fraudes Concernant les Denrées Alimentaires. ("Second International Congress for the Repression of Frauds connected with Foods"). Paris: Société Universelle de la Croix-Blanche de Genève.

THIS pamphlet is a section of the programme of the Food Congress held in Paris from October 17th to 24th. It contains details of the proposals made for the standards to which drugs, essential oils, and chemical products should attain. The limits of purity suggested are fairly wide, but at the same time not wide enough to include fraudulently adulterated or very poor specimens, and the adoption of the standards would certainly tend to reduce adulteration and to aid the druggist in procuring reliable and active preparations.

Outlines of Chemistry with Practical Work. By HENRY JOHN HORSTMAN FENTON, M.A., Sc.D., F.R.S. First Part. Cambridge: The University Press. 1909.

As a summary of the results discussed at greater length in larger text-books of physical chemistry, or as a guide to their use, this book will prove a boon to the student who is pressed for time in his chemical work. The author writes more particularly for candidates for the Natural Science Tripos, who have to acquire a fairly considerable knowledge of chemistry, and yet can frequently give but one complete year to the task. The use of one of the larger and more complete treatises is out of the question, but, on the other hand, the candidate has to have some acquaintance with practically every branch of the subject treated in such books, and superficiality is fatal. To make extracts is tedious and difficult, and as a general rule it is found far more satisfactory to use a less detailed book as a foundation and to supplement it than to rely upon the reading of extracts. This book, then, is intended to provide the necessary summary both of theoretical and practical work in general chemistry. It is a scholarly treatise, not by any means easy reading, but stimulating to the enthusiast. The practical work illustrating each chapter is particularly good, and there is ample material to occupy many hours of laboratory practice. The book will be acceptable also to teachers to form a basis for preparing lectures on general chemistry, and they will find that some of the chapters are remarkable both for their lucidity and for the breadth and impartiality of treatment displayed in them.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlix., Nos. 12 and 13, September 20 and 27, 1909.

These two numbers contain no chemical matter.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xlii., No. 13, 1909.

Action of Caustic Potash on Aniline.—A. Bacovescu.—When colourless freshly distilled aniline is intimately mixed with powdered caustic potash the mixture becomes slightly warm and turns reddish brown. The reaction is at its maximum when one part of aniline is present to twelve parts of alkali. The products of the reaction are azobenzene and *o*-oxy-azobenzene, $\text{HO.C}_6\text{H}_4.\text{N}:\text{N.C}_6\text{H}_5$. Caustic potash also acts on azobenzene and converts hydrazobenzene into azobenzene. Azobenzene is also prepared when KMnO_4 acts on aniline, or when aniline is oxidised in alkaline solution by hypochlorite. Probably oxidation by the oxygen of the air takes place in the experiments described above, and the caustic potash merely induces the reaction.

Synthesis of Papaverine.—Amé Pictet and Alfons Gams.—The authors have shown that papaverine can be synthesised from veratrol and vanillin by a series of reactions which lead to the formation of amino-acetoveratronhydrochloride from veratrol, and of homoveratroylchloride from vanillin. These two compounds unite to form homoveratroyl-amino-acetoveratron with loss of two molecules of hydrochloric acid, and from this papaverine is readily obtained by oxidising and then removing two molecules of water.

Anodic Formation of Hydrogen Peroxide.—E. H. Riesenfeld and B. Reinhold.—When caustic potash solution is electrolysed at any temperature lying between 0° and -60° , a considerable amount of hydrogen peroxide is formed according to the equation $2\text{OH}^- + 2(+)=\text{H}_2\text{O}_2$. If caustic soda is substituted for caustic potash no hydrogen peroxide is formed. This must be explained by assuming that caustic soda decomposes H_2O_2 catalytically more strongly than caustic potash, and, moreover, the potential of platinum in caustic potash is higher than in caustic soda. The optimum of the formation of hydrogen peroxide occurs at -40° . In these experiments it was observed that the anode solution became yellow owing to the formation of potassium ozonate.

Action of Calcium Oxide on Hydrazine Hydrate.—Arthur Stähler.—When hydrazine hydrate is mixed with lime, heat is generated, and when the product is heated hydrazine distils over first; then as the temperature rises some ammonia is found mixed with the hydrazine. The mechanism of the reaction has not yet been explained. Either a solid solution of hydrazine in calcium oxide or hydroxide is formed, or else a compound $\text{Ca}(\text{ON}_2\text{H}_5)_2$ according to the equation $2\text{CaO} + 2\text{N}_2\text{H}_5(\text{OH}) = \text{Ca}(\text{ON}_2\text{H}_5)_2 + \text{Ca}(\text{OH})_2$. At a moderate temperature this compound dissociates into $\text{Ca}(\text{OH})_2$ and N_2H_4 , and at higher temperatures nitrogen and ammonia are formed.

Action of Magnesium Organic Compounds on Boric Acid Esters.—Eugen Khotinsky and M. Melamed.—Magnesium organic derivatives of the aromatic and aliphatic series act on different esters of boric acid in the same way as on those of silicic acid, but the reaction is much more rapid and the products are more easily obtained in the pure state. Only one alcoholic residue of the boric acid ester can be replaced,

$R.Mg.X + R'.O.B(OR')_2 = R.B(OR')_2 + R'.O.Mg.X$. The aliphyl and aryl boric acid esters are readily saponified by cold water. When boric acid methyl, ethyl, or propyl esters are used the corresponding boric acids are obtained directly, and the esters need not be isolated, but in the case of the isobutyl and isoamyl esters the boric acid esters are saponified only at the temperature of the water-bath. The best yield of aryl-boric acids was obtained with boric acid isobutyl ester. The aliphyl-boric acids are very unstable and volatile. Methyl-boric acid, $CH_3.B(OH)_2$, has not yet been prepared in the pure state, owing to its great instability.

Determination of Phosphoric Acid in Acid Solution with Alkaline Molybdate Solution and Glue.—A. Grete. Phosphoric acid can be determined in acid solution by mixing with a solution of glue, adding ammonium nitrate and nitric acid, boiling, and allowing molybdic acid solution to drop into the mixture from a burette until a distinct precipitate remains. The solution is again boiled and well shaken, when a compact yellow precipitate settles. More molybdate is added, and the mixture is again boiled until the addition of molybdate no longer produces a precipitate. From the volume of molybdic solution thus used the percentage of phosphoric acid in the original solution can be calculated. The molybdic acid solution is prepared by adding a concentrated solution of molybdic acid in ammonia to nitric acid till the precipitate obtained does not dissolve, and adding ammonia. It is then titrated with a KH_2PO_4 solution; 1 cc. of solution should equal 0.0025 gm. P_2O_5 . The ammonium nitrate-nitric acid solution contains 200 grms. of ammonium nitrate and 26.5 cc. of nitric acid (sp. gr. 1.197) in 1 litre. The solution of glue has to be carefully made by allowing glue to stand in cold water, then pouring off the water and boiling with water and nitric acid; after cooling, the solution is made ammoniacal and any phosphoric acid present is precipitated with magnesia mixture. Then ammonium carbonate is added, and portions of the solution are filtered off as required.

Lecture Experiment to show Velocity of Reaction.—W. Nernst.—If about 0.001N barium hydroxide solution is added to methyl formate and a trace of phenolphthalein, instant change of colour is observed. With litmus, cyanine, β -nitrophenol, and methyl-orange the times required at 18° are about one, fifteen, thirty, and one hundred and twenty minutes. These results can be used to demonstrate the velocity of hydrolysis of the ester.

Equilibrium of Hydrochloric Acid.—Alfred Coehn and Alexandra Wassiljewa.—Hydrochloric acid gas perfectly free from traces of air or oxygen was exposed to the action of the light from a mercury quartz lamp in order to ascertain whether it was decomposed into hydrogen and chlorine. It was found that the decomposition was effected so rapidly that even after a quarter of an hour 1½ to 2 cc. of hydrogen could be collected and exploded with air. The reaction occurs only in ultra-violet light. The value of the constant of equilibrium was found to be $K = 6.25 \times 10^{-6}$, corresponding to a decomposition of 0.25 per cent of hydrochloric acid.

Reduction of Titanium Tetrachloride by Hydrogen.—Hans Goerges and Arthur Stähler.—Titanium tetrachloride is reduced to the trichloride by hydrogen at temperatures ranging from 785—1200°, the yield of $TiCl_3$ being increased as the temperature is raised, although the reaction is not quantitative even at 1200°. $TiCl_3$ is a fine reddish violet powder which is rapidly decomposed by damp air. Even at the ordinary temperature it decomposes according to the equation $2TiCl_3 \rightleftharpoons TiCl_2 + TiCl_4$. Solutions of titanium dichloride (divalent titanium) turn violet when heated in air or when treated with nitric acid, the colour in the latter case disappearing. With $TiCl_4$ they give a violet coloration, and with ammonia, ammonium carbonate, or ammonium sulphide a brownish black precipitate. The authors have also found that divalent titanium gives a green solution with potassium rhodanide,

green titanous acetate with sodium acetate, and calomel with mercuric chloride. On evaporation *in vacuo*, crystals probably of $TiCl_2 \cdot xH_2O$ are obtained.

General Reaction of Aldehydes and Ketones.—Hartwig Franzen.—When an aqueous solution of calcium cyanide is shaken with benzaldehyde a colourless crystalline powder is produced, according to the equation $2C_6H_5.C \begin{smallmatrix} O \\ \parallel \\ H \end{smallmatrix} + Ca(CN)_2 = C_6H_5.CH \begin{smallmatrix} O \\ \parallel \\ CN \end{smallmatrix} \begin{smallmatrix} O \\ \parallel \\ CN \end{smallmatrix} \begin{smallmatrix} O \\ \parallel \\ CN \end{smallmatrix} + CH_3.C_6H_5$. This formation of calcium compounds of cyanhydrines seems to be a general reaction given by a whole series of aldehydes and ketones. Acetophenone, however, forms no solid compounds with calcium cyanide. Similar compounds are obtained with barium, strontium, and magnesium cyanides. The benzaldehyde compound is decomposed by hot water into benzaldehyde and calcium cyanide. It is only very slightly altered by boiling with alcohol.

Ethylene Ozonide.—C. Harries and Rudolf Koetschau.—When ozone acts on propylene the ozonide of formula $CH_3.CH \begin{smallmatrix} O \\ \parallel \\ O \end{smallmatrix} CH_2$ is obtained if the concentration of ozone in the current of oxygen employed is too great. If only 7 per cent ozone is used the ozonide, $CH_2-CH_2 \begin{smallmatrix} O \\ \parallel \\ O \end{smallmatrix}$, may be prepared from ethylene. It is a perfectly stable though extremely explosive substance. From determinations of the molecular weight and molecular refraction it is found that it is the normal ozonide of formula $CH_2-CH_2 \begin{smallmatrix} O \\ \parallel \\ O \end{smallmatrix}$.

MISCELLANEOUS.

Society of Dyers and Colourists.—The London Section proposes to hold early in December an "Open Night," when members are requested to bring forward matters for general discussion. The subject of same should be sent to the Hon. Secretary, M. C. LAMB, the Leathersellers' College, Tower Bridge Road, S.E.

Potassium Permanganate as a Test for Morphia.—I have found the above reagent to give a characteristic colour test with morphia hydrochloride. A drop of weak permanganate solution and one of morphia hydrochloride, both in distilled water, give a distinct yellow. With aconite the same method of testing with permanganate solution gave indications of a green coloration, whilst with belladonna no distinct colour reaction was obtainable.—J. C. THOMLINSON.

MEETINGS FOR THE WEEK.

MONDAY, Nov. 1st.—Royal Institution, 5. (General Monthly Meeting). Society of Chemical Industry, 8. "Technical Gas Calorimetry," by J. H. Coste. "On Naphthalene Picrate and the Quantitative Determination of Naphthalene," by W. P. Jorissen and J. Rutten. "Manufacture of Large Blocks of Artificial Stone from Sand and Lime," by J. C. Stead.

WEDNESDAY, 3rd.—Society of Public Analysts, 8. "Detection and Estimation of Small Quantities of Antimony," by P. Schidrovitz and H. A. Goldsbrough. "Phosphates in certain Vinegars and in the Materials Used in their Manufacture," by T. Fairley. "Determination of Essential Oils in Spices and Aromatic Drugs," by R. A. Cripps and J. A. Brown. "Note on Holde's Test, and the Detection of Paraffin Wax in Lard and other Fats," by H. Dunlop.

THURSDAY, 4th.—Chemical, 8.30. "Dynamics of the Reaction between Iodine and Acetone," by H. M. Dawson and Miss M. S. Leslie. "Formation and Reactions of Imino-compounds—Part XI., Formation of 1-Imino-2-cyanocyclopentane from Adiponitrile," by J. F. Thorpe.

FRIDAY, 5th.—Physical, 8.

THE CHEMICAL NEWS.

VOL C., No. 2606.

A COLORIMETRIC METHOD FOR THE ESTIMATION OF SMALL QUANTITIES OF VANADIUM.

By ARNOLD WILLIAM GREGORY, B.Sc. (Lond.).

MANDELIN's reagent (a solution of vanadic oxide in sulphuric acid) is in general use for the detection of alkaloids. With strychnine this reagent gives a violet coloration which gradually changes to an orange tint.

Inversely, the author has found that a solution of strychnine in concentrated sulphuric acid not only affords a means of detecting small quantities of vanadium in the presence of titanium, molybdenum, and tungsten, but also may be used in the quantitative estimation of that element.

The solution of strychnine used contains 4 grms. of pure strychnine in a litre of concentrated sulphuric acid.

A standard solution of vanadium is made by dissolving 0.1778 gm. vanadic oxide in 10 cc. of concentrated sulphuric acid, and diluting to litre (1 cc. of this solution contains 0.0001 gm. vanadium).

To a measured portion of the solution to be tested 20 cc. of concentrated sulphuric acid are added, together with a small crystal of potassium chlorate to oxidise the vanadium to V_2O_5 . The solution is evaporated until white fumes of sulphuric acid are given off and chlorine dioxide is no longer evolved.

A measured quantity of the standard vanadium solution is treated in an exactly similar manner.

When the solutions are quite cold, 20 cc. of the strychnine solution are added to each. A deep violet colour is at first produced, which changes gradually to an intense orange. The solutions are allowed to stand for ten minutes, by the end of which time no further change is visible. The colours are then compared by transferring the solutions to stoppered comparison tubes of similar dimensions, the beakers being rinsed out with a little concentrated sulphuric acid.

The solution showing the more intense colour is then diluted with concentrated sulphuric acid until no difference of tint is discernible in the two tubes when viewed against a semi-opaque white glass screen.

Since the amount of vanadium in the measured quantity of the standard solution is known, the amount in the other tube can be calculated by comparing the heights of the solutions in the two tubes. It is more accurate to proceed in this manner than to compare the volumes of the solutions, as any error due to the irregularities in the bore of the comparison tube is eliminated.

A convenient comparison tube is one 12 inches long and $\frac{3}{4}$ inches internal diameter.

Using such a tube a convenient colour for comparison is obtained by 0.0005 gm. of vanadium diluted until it occupies about half the volume of the comparison tube.

The best results are obtained when the amounts of vanadium in the two solutions compared are approximately the same. It is advisable therefore, if there is a wide difference in the colours in a preliminary test, to make a second test, using such quantities that the tints approximate.

The presence of large quantities of titanium, molybdenum, tungsten, or aluminium do not affect the test.

Iron, if present, must be removed, as in large quantities it entirely prevents the formation of the colour. When iron is present the substance to be tested should be fused with sodium carbonate, extracted with water, and filtered. The filtrate is then made up to a definite volume and a measured portion tested as described above.

If the strychnine solution is added to an aqueous solution

of a vanadic salt, the colour produced is less intense. It is therefore necessary to carry out the tests under exactly similar conditions to those indicated above.

It is essential that the vanadium should be in the highest state of oxidation (V_2O_5), as salts of the lower oxide (V_2O_4) do not give the colour test.

Experimental.

A standard solution of vanadic oxide was prepared, containing 0.1778 gm. per litre (1 cc. = 0.0001 gm. vanadium).

Varying quantities of vanadic oxide were then taken, and the test carried out as described in the foregoing, 10 cc. of the standard solution being treated similarly for comparison. The standard was diluted with strong sulphuric acid until the height of the solution in the comparison tube was 15 cm.

The first column shows the quantity of vanadium taken in each case; the second the height in the comparison tube of the solution to be tested, when of similar tint to the standard; the third the quantity of vanadium calculated.

Quantity of V taken.	Height of sol. (cm.).	V calculated.
0.0010	14.8	0.00099
0.0012	18.1	0.00121
0.0015	22.2	0.00148
0.0020	29.5	0.00197

In order to test the permanency of the colour the test was carried out with 0.001 gm. vanadium, and the solution, after diluting to the 15 cm. mark, was allowed to stand in the comparison tube three hours. At the end of that period a similar quantity of vanadium was treated in the same manner. The tints in the two tubes were identical.

A quantity of vanadic oxide (0.100 gm.) was then fused with sodium carbonate. The mass was dissolved in water, and made up to 250 cc. The test was then carried out in portions of 5 cc. of this solution, 10 cc. of the standard solution being used for comparison. The standard was diluted to 15 cm. It was found necessary to dilute the test solution in three experiments to 16.9 cm., 16.7 cm., and 16.6 cm., respectively. Mean, 16.73 cm. Vanadium present in 0.100 gm. of V_2O_5 :—

$$\frac{0.001 \times 16.73 \times 250}{15.0 \times 5} = 0.05575 \text{ gm.}$$

$$\text{Theoretical} = 0.05623 \text{ gm.}$$

A solution of titanium sulphate was made by dissolving 0.100 gm. titanium oxide in concentrated sulphuric acid. To this 10 cc. of the standard vanadium solution were added. The test was then carried out, and the colour compared with that produced by a similar quantity of the standard vanadium solution alone. At similar dilutions the tints were found to be identical. Similar results were obtained when the test was carried out in the presence of molybdenum and tungsten.

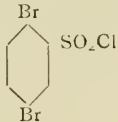
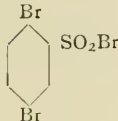
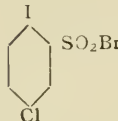
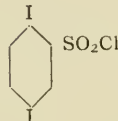
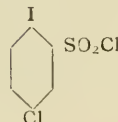
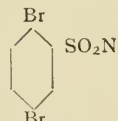
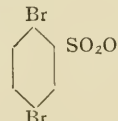
A mixture was prepared of 0.010 gm. vanadic oxide, 0.010 gm. molybdenum trioxide, 0.010 gm. tungsten oxide, and 1 gm. of vanadium free iron ore. The mixture was then fused with 10 grms. of sodium carbonate. The mass was extracted with water, filtered to remove iron oxide, &c., and made up to 500 cc. A measured quantity (100 cc.) was taken, at 20 cc. strong sulphuric acid added, together with a little potassium chlorate, and the solution was then evaporated until white fumes appeared. After cooling, the test was carried out as before, using 10 cc. of the standard vanadium solution for comparison. It was found necessary to dilute the test solution to 16.5 cm. The total amount of vanadium taken was calculated.

$$\frac{0.001 \times 16.5 \times 500}{15.0 \times 100} = 0.0055 \text{ gm.}$$

$$\text{Theoretical} = 0.0056 \text{ gm.}$$

THE STUDY OF ISOMORPHOUS DERIVATIVES
OF BENZENE SULPHONIC ACID.*

IN continuance of previous work, a number of members of several series of sulphonic derivatives of para-dihalogen derivatives of benzene have been prepared and crystallographically examined. The substances for which data are given below crystallise in the monosymmetric system:—

	$a : b : c$	M.p.
1. 	2.4760 : 1 : 1.1439, $\beta = 95^\circ 26'$	71°
2. 	2.4792 : 1 : 1.1448, $\beta = 96^\circ 49'$	114°
3. 	2.4689 : 1 : 1.1537, $\beta = 95^\circ 50'$	102°
4. 	0.8552 : 1 : 0.6676, $\beta = 95^\circ 22'$	132°
5. 	0.7288 : 1 : 0.6544, $\beta = 99^\circ 42'$	69°
6. 	0.9576 : 1 : 0.8361, $\beta = 99^\circ 30'$	143°
The following compound crystallises in the orthorhombic system:—		
7. 	0.8904 : 1 : 0.8357	106°

The substances numbered 1, 2, and 3 form a well-defined isomorphous series, as is immediately indicated by the close approximation of the axial ratios quoted. The compounds 4 and 5 differ entirely in crystalline character from the foregoing, but the similarity of the ratio c/b in the two cases suggests an intimate morphotropic relation as existing between their crystalline structures.

In a series of papers Barlow and Pope have pointed out that the whole space occupied by a crystalline substance can be conveniently regarded as parcelled out amongst

the various atoms composing the material, and have shown that this mode of treatment leads to the conclusion that the volumes thus allocated to atoms of different elements are, in any one substance, approximately proportional to their valencies. A crystalline substance is thus to be regarded as a close-packed assemblage of spheres of atomic influence, in which each of the latter has a volume directly proportional to the fundamental valency of the atom which it contains. The close-packed assemblages referred to are geometrically partitionable into units representing individual molecular aggregates, and these should represent in composition, constitution, and configuration the chemical molecules of the substances concerned.

From the study of the crystalline forms of benzene and its derivatives Barlow and Pope have deduced a form of assemblage for the hydrocarbon which is partitionable into units of the composition, C_6H_6 , and have described the configuration of the molecule as thus derived. In the crystalline assemblage the carbon spheres of influence are arranged in columns, of which each link consists of three spheres in triangular contact, and it has been concluded that these columns remain intact in the crystalline derivatives of benzene; the passage from the hydrocarbon to any derivative thus involves the moving apart of the columns of carbon spheres and the insertion of the substituting groups in the spaces thus provided.

It is possible to test the correctness of the conclusions briefly referred to above by aid of crystallographic data for benzene derivatives. Compounds may be compared by means of their "equivalence parameters, which are the linear dimensions of parallelepipeds having volumes represented by the sums, W , of the valencies of the atoms composing the respective molecules, those linear dimensions being proportional to the crystallographic axial ratios. For benzene itself, which crystallises in the orthorhombic system with $a : b : c = 0.891 : 1 : 0.799$, the value of W is 30, and the equivalence parameters are calculated from these data as $x : y : z = 3.101 : 3.480 : 2.780$.

The last of these values, $z = 2.780$, represents the height of two links in the columns of carbon spheres in the crystalline hydrocarbon, and if, as has been suggested, these columns remain intact in the crystalline derivatives of benzene, the value 2.780 should recur amongst the equivalence parameters of the derivatives. This has been already shown to be the case in a long series of crystalline derivatives of picric and styphnic acids, and the data now contributed enable the conclusion to be extended to the sulphonic derivatives of benzene described above.

The following table gives the equivalence parameters, x , y , and z , and the valency volumes, W , for the substances numbered in the above table of axial ratios:—

1.	$W = 36.$	$x : y : z = 5.787 : 2.337 : 2.674, \beta = 95^\circ 26'.$
2.	36.	$5.796 : 2.338 : 2.676, \beta = 96^\circ 49'.$
3.	36.	$5.761 : 2.333 : 2.692, \beta = 95^\circ 50'.$
4.	36.	$3.409 : 3.986 : 2.661, \beta = 95^\circ 22'.$
5.	36.	$3.095 : 4.247 : 2.779, \beta = 99^\circ 42'.$

The third equivalence parameter, z , calculated from the axial ratios and the valency volumes, in each case approximates to the corresponding value, $z = 2.780$, for benzene itself. The corresponding value in the case of the series of picric and styphnic acid derivatives examined by Jerusalem varies between 2.660 and 2.788 (*Trans. Chem. Soc.*, July, 1909, p. 1275).

The axial ratios of the more complex benzene derivatives represented by the labile form of 1 : 4-dibromobenzene-2-sulphanilide and the ethylic 1 : 4-dibromobenzene-2-sulphonate do not, in the form stated above, immediately yield values approximating to 2.780 amongst their equivalence parameters. On dividing unit length along the axis b by 2 in the former case and multiplying it by 2 in the latter, the following equivalence parameters are, however, obtained in which the value 2.780 recurs:—

6.	$W = 68.$	$x : y : z = 5.327 : 2.782 : 4.653, \beta = 99^\circ 30'.$
7.	49.	$= 2.859 : 6.410 : 2.679, \beta = 90^\circ 0'.$

* Report of the Committee, consisting of Principal Miers (Chairman), and Professors H. E. Armstrong (Secretary), W. J. Pope, and W. P. Wynne. Read before the British Association (Section B), Winnipeg Meeting, 1909.

The confirmation of Barlow and Pope's conclusion as to the existence of the columns of carbon spheres in crystalline benzene derivatives, which Jerusalem obtained by the study of the picrates and styphnates, may consequently be extended to the quite different class of derivatives dealt with in this Report.

The Committee are indebted to Messrs. Colgate, Rodd, and Runecles for assistance they have rendered in preparing and measuring compounds described in this Report.

TANTALUM AND ITS INDUSTRIAL APPLICATIONS.*

By ALEXANDER SIEMENS, M.Inst.C.E.

WHEN the announcement was made in the year 1878 that "the division of the electric light had been successfully accomplished," many people believed that the days of lighting by gas had come to an end, and acted accordingly, much to their own disadvantage: for the competition of the glow-lamp served only to stimulate its rival to new life.

Burners of improved construction, regenerative burners, and finally gas mantles, helped to restore to gas the ground it had lost, and until a short time ago even threatened to check the spreading of electric lighting.

Not only this growing competition of gas, but the universal necessity of cheapening the production of commodities that are for general use, forced electric engineers to study in all aspects the question of improving the efficiency of electric lighting.

As a guide in their researches, they had the well-known principle that the illuminating power of a solid body increases at a much greater ratio than its temperature, or, in other words, that with the increase of temperature a greater percentage of the energy expended for heating the body is converted into light.

There is plenty of room for improvement; for even the most economical source of light, the electric arc lamp, converts only about 1 per cent of the energy of the electric current flowing through it into light, the rest appearing as heat, so that in reality all methods of lighting devised by men are, to a much greater extent, methods of heating.

The first successful incandescent lamp consisted of a carbon filament; and for a long time carbon appeared to be the only suitable substance, although the temperature at which such a filament can be raised is limited to about 1600° C., as above this point the carbon begins to disintegrate rapidly.

At this temperature the lamp consumes from three to three and a-half watts per candle-power, while any attempt to produce light more economically, by raising the temperature of the filament results only in shortening its life, and destroying thereby its power of competing with gas lighting.

An improvement on this result was introduced by Prof. Nernst, of Göttingen, who suggested as the source of light refractory earths, similar in character to those used for gas mantles, which, however, conduct electricity only when they are hot.

Lamps constructed on Prof. Nernst's principle have therefore to be fitted with contrivances for heating their filaments when starting, which complicate the construction of the lamp.

Another step forward was made by the invention of the osmium lamp, which is produced in a somewhat similar manner to the carbon lamp, by squirting a plastic mixture of metallic oxide and a reducing agent into the shape of a filament, which is gradually heated in a glass bulb by the passage of an electric current, while the bulb is being exhausted by an air-pump or an equivalent device.

As far as utilisation of energy goes, these lamps are a great improvement on carbon lamps, but their filaments are very brittle; and the total production of osmium per

year is only about 8 kg. for the whole world, of which 5 kg. are wanted for medical purposes.

In January, 1905, Dr. W. von Bolton, the head of the chemical laboratory of the firm of Siemens and Halske, announced in a lecture to the Elektrotechnische Verein of Berlin, that he had succeeded in producing pure tantalum, and his discourse was followed by Dr. O. Feuerlein, describing how tantalum had been utilised for filaments in the lamp-works of the firm.

These discourses presented the result of long years of research work, based on the general principle already alluded to, that that filament would give the best economical results which could be maintained for the longest time at the highest temperature.

The number of substances capable of conducting electricity and of sustaining such high temperatures is very limited, and platinum, the most refractory of the well-known metals, had been tried and found wanting.

It became therefore necessary to start the research by devising methods for producing the rare metals in a commercially possible manner, and then try one after the other as filaments of incandescent lamps.

While working on these lines, Dr. von Bolton succeeded, in the first instance, in producing a vanadium filament by heating a mixture of vanadium pentoxide and paraffin to 1700° C., and thereby producing sticks of vanadium trioxide, which in their turn were heated by electric currents in a glass bulb exhausted by an air-pump, and so converted into metallic filaments.

As it was found that vanadium melts at about 1680° C., such filaments were no improvement on carbon filaments; and the next substance to be investigated was niobium, which belongs to the same group of elements, but has nearly double the atomic weight.

Treated in a similar manner, the niobium filament gave somewhat better results, but still its melting-point, estimated at 1950° C., was too low for practical purposes.

In this connection it should not be forgotten that, at a temperature considerably below their melting-point, all these metals begin either to soften or to disintegrate, so that their "working" temperature is not identical with their melting temperature.

Turning his attention to tantalum, which has an atomic weight of 181, Dr. von Bolton experimented with the black metallic powder produced by the method of Berzelius and Rose, and found that it could be rolled into a fairly coherent mass in the form of ribbons.

Alternative experiments, conducted on the lines by which vanadium and niobium had been obtained, resulted in the production of pure tantalum in the form of a metallic button, which was found to be tough and malleable like steel.

These and other qualities convinced Dr. von Bolton that nobody before him had handled pure tantalum, although Berzelius had first obtained the metal by a chemical process in 1824, and later Moissan succeeded, in 1902, in producing it in his electric furnace.

The latter describes tantalum as a hard brittle metal of the specific gravity of 12.8 and a non-conductor of electricity, but he adds that the substance obtained by him contained about a half per cent of carbon.

Considering the high atomic weight of tantalum, this admixture of carbon evidently exercises a great influence on the physical qualities of tantalum, and explains the differences between the observations of Dr. von Bolton and those of his predecessors.

In nature ores containing tantalum are found in many places, principally in Scandinavia, North America, South-west Africa, and Western Australia.

A specimen of columbite from South Dakota and another of tantalite from Western Australia are exhibited.

The columbite contains from 10 to 40 per cent of tantalum pentoxide, Ta₂O₅, and a good deal of niobium combined with iron and manganese in various proportions.

As the separation of tantalum and niobium is somewhat troublesome, it is preferable to utilise the tantalite, which

* A Discourse delivered before the Royal Institution, April 23, 1909.

consists almost entirely of iron and manganese combined with tantalum pentoxide.

From these ores tantalum is separated in the form of a fluoride in combination with potassium, K_2TaF_7 , and subsequently reduced by metallic potassium to the black powder already mentioned, which, however, still contains some oxide and some hydrogen.

In order further to purify the product, the powder is pressed into the form of small cylinders (one of which is on the table), which are melted in a vacuum by an electric current under certain precautions into small buttons of pure tantalum such as are exhibited.

Since the production of tantalum has been carried out on a commercial scale, it has been possible to improve many details of the process, so that the tantalum produced by it at the present time is even purer than that shown in 1905 at the discourse of Dr. von Bolton and Dr. Feuerlein.

Some specimens of this latest tantalum have been submitted to Sir James Dewar, who has very kindly made experiments with reference to its specific heat and to its thermal conductivity.

He ascertained the specific heat by plunging small spheres of tantalum, which had been heated to the temperature of boiling water, into water of $14^\circ C.$, then transferring them to melting carbonic acid ($-78^\circ C.$), and finally to liquid air ($-183^\circ C.$), and as an average of several experiments the specific heat was found to be between—

$100^\circ C.$	and	$14^\circ C.$	$= 0.033$
$14^\circ C.$	"	$-78^\circ C.$	$= 0.032$
$-78^\circ C.$	"	$-183^\circ C.$	$= 0.028$

while Dr. von Bolton in 1905 gave the specific heat as 0.0363.

Multiplying these results by the atomic weight (181) it will be seen that Dr. von Bolton's value (6.57) is slightly higher, and Sir James Dewar's value (5.97) lower than 6.4, which, according to Dulong and Petit, is the atomic specific heat.

By the kindness of Sir James, his experiment for showing the relative thermal conductivity of iron, copper, and tantalum can be repeated here by dropping three short rods, made of these metals, in liquid air, while their tops, above the cardboard cover, are exposed to the air of the room.

In a short time the moisture of the air condenses on the rods and freezes to a distance, which depends on the conductivity of each metal.

The results of Sir James Dewar's experiments prove tantalum to have about three-quarters the conductivity of iron and about one-eighth the conductivity of copper.

At ordinary temperatures, say, below $300^\circ C.$, pure tantalum resists the action of all acids, except fluoric acid, of all alkalis, and of moisture, so that it is an ideal material for chemical apparatus which do not require high temperatures, and for any implements which, when made of steel, are liable to rust.

It has already been stated that pure tantalum is tough and malleable, so that it can be hammered out into thin sheets or drawn into fine wire, the diameter of the filament wire being 0.03 mm. or about one-eight-hundredth of an inch; all the same, it is elastic and as hard as soft steel, and has a tensile strength of 93 kg. per square mm., which is equal to 57 tons per square inch.

This means that the filament wire is capable of supporting about 80 grms., or 2.8 ounces, as can be shown by actual experiment.

Tantalum sheet can be stamped into various shapes, and out of bars of tantalum springs can be bent, as the specimens on the table show.

Another use made of tantalum is as material for writing pens, manufactured in the usual way.

When it was first offered for this purpose, it was found that the material could not pass the test prescribed for pens made of steel.

These are pressed by a weight of 180 grms. on writing

paper, which is moving at the same speed as ordinary writing, and while 10 km. (6½ miles) of paper are passing the loss by abrasion must not exceed 0.7 mg. (0.01 grain).

At first the tantalum pens lost more than double the permitted weight, but it was found that slightly oxidising the surface of the pens hardens them so much that they only lose 0.8 mg. by the 10 km. test.

By weight this is still more than permitted for steel pens, but having regard to the specific weights of the two substances, the actual volumetric abrasion of the tantalum pen is the lesser of the two.

Although only the surface of the pens had been oxidised, it was found that the rate of abrasion remained the same for the whole length of 10 km., when it was expected that this rate would increase materially after the skin of oxide had been ground off.

Advantage was taken of this circumstance when an inquiry was received from India whether it would be possible to manufacture cataract knives for oculists out of tantalum.

The qualities demanded of such a knife are that its blade should be:—

1. Intensely hard, so as to be able to acquire a very sharp edge of great smoothness, and to retain this fine edge for a long time.
2. Very tough without any tendency to bend.
3. Chemically and mechanically stable, so that it can be easily sterilised and that it is not liable to rust.
4. Capable of acquiring a high polish.

Manufacturing such a blade out of pure tantalum and slightly oxidising it, before polishing it, appears to fulfil these stringent conditions, but as the knife which is on the table has not yet been actually tried for an operation, it can only serve to demonstrate the similarity of tantalum to steel for such purposes.

Another field for the application of tantalum may be found in the supply of dental instruments, owing to its immunity from chemical changes, but beyond showing two cases of such appliances, there is no necessity to go further into details.

While possessing all these qualities of a true metal, tantalum has some others which rather limit its usefulness.

When heated to a dull red it absorbs gases greedily, especially hydrogen and nitrogen, and by combining with them it loses its tensile strength and becomes brittle.

Here are three pieces of tantalum wire taken from the same coil; one of them has been heated in an atmosphere of nitrogen, the other in hydrogen, and the third has not been interfered with. The consequence is that the latter has retained its strength, while the former have become brittle and useless.

On heating tantalum in air, it shows first a yellow and then a blue tint like steel, but when the heating is continued it burns to pentoxide.

The black powder and thin wires can even be lighted by applying a match to them, as the experiment shows.

Its melting-point, *in vacuo*, lies between $2250^\circ C.$ and $2300^\circ C.$, which makes it particularly suitable for electrodes in vacuum-tubes, especially as it does not disintegrate—for example, Ta electrodes are extensively used in Röntgen tubes—and its specific weight is 16.6.

Turning now to the electrical qualities of tantalum, its specific resistance was stated by Dr. von Bolton, in 1905, to be on the average 0.165, with a temperature coefficient of 3 per cent between 0° and 100° Celsius.

Further experiments conducted by Dr. Pirani in the laboratory of Siemens and Halske revealed the fact that wires of various thicknesses varied in their specific resistance from 0.173 to 0.188; but after they have been heated to 1900° Celsius in a high vacuum for from 100 to 200 hours, they all possessed the same specific resistance, viz., 0.146, and their temperature coefficient between 0° and 100° Celsius had risen to 0.33 per cent.

As a temperature of the tantalum filament, when consuming 1.5 watt per candle-power, is about $1850^\circ C.$, and

its resistance about six times its resistance at 100° C., the temperature coefficient between 100° and 1850° C. may be taken, on the average, as 0.29 per cent.

No doubt the difference between these results is caused by alterations in the structure of the wires during their manufacture, and the heating *in vacuo* served a similar purpose to the annealing of steel, so that Dr. Pirani's results published in 1907 may be taken as standards.

At present the most important industrial application of tantalum is its use for the filaments of incandescent lamps, which may be said to date from July, 1903, when Dr. Feuerlein had succeeded in producing a tantalum wire one-twentieth of a mm. in diameter. Of this wire he made a glow-lamp with a filament 54 mm. long, using a current of 9 volts 0.58 ampère, and giving a light of 3.5 candles (Hefner), at the rate of 1.5 watt per candle-power.

A simple calculation shows that for a current of 110 volts, 660 mm. of the same wire would be required, giving at the same rate of consumption of energy a light of 43 candles.

In carbon lamps for 220 volts the length of filament is only 400 mm., and the filaments remain hard until they disintegrate. Tantalum filaments, like other metallic filaments, soften, however, to such a degree that they cannot be used in the same shape as carbon filaments.

After trying various methods of housing the long Ta filament in a glass bulb of approximately the same dimensions as the carbon glow-lamps, the present form was arrived at during the year 1904. In this lamp, which was adopted as standard, the length of the filament was 650 mm., its diameter 0.05 mm., and its weight 0.022 gm., so that about 45,000 of these lamps contain 1 kg. of Ta.

Since then these dimensions have been modified to a certain extent; for instance, the diameter of the filament is now only 0.03 mm., but the external shape has not been altered.

It was soon found that after burning a short time the filament underwent certain structural changes and lost its great tensile strength. Examination under a microscope revealed the fact that in about 1000 hours the smooth cylindrical filament shows signs of capillary contraction, as if the cylinder was going to break up into a series of drops, and the surface, from being dull, commences to glitter. This contraction of the filament after being heated is readily recognised by comparing a new lamp with an old one. On the stars of the new lamp the filament hangs loosely, while in the old lamp the filament is evidently in tension.

The characteristic difference between carbon filaments and tantalum filaments is shown by a diagram representing the influence of temperature on the electric resistance of the two filaments in proportion to each other.

In order to have the differences at once shown in per cents, the normal pressure and the normal resistance of both filaments, when giving the light of 1 candle for 1.5 watt, is marked as 100, and it is immediately seen that the resistance of Ta alters directly, and that of carbon inversely as the temperature. Owing to this quality, a Ta filament is better able to resist overheating than a carbon filament, as the following experiment shows, where two lamps, one Ta and one C, burning normally at 110 volts with 1.5 watt per candle power, are gradually exposed to higher voltages. The C lamp breaks while the Ta lamp stands up to 200 volts, the highest voltage available to-night. Of course its useful life will be shorter than at its normal voltage.

As stated at the beginning of the discourse, the primary object of all the research was to find a filament more economical in the consumption of electrical energy than the C filament, and the following experiments will show that the Ta filament is, in this respect, a great improvement on the C filament.

To begin with, a comparison can be made by burning a Ta and a C lamp under water, each being immersed in a vessel containing the same quantity of water.

Owing to the C lamp requiring more energy to give the same light as the Ta lamp, the temperature of the water in the C vessel rises quicker than in the other vessel.

Another way of showing the difference is by measuring the current taken by each of the two lamps when giving approximately the same light, or by sending the same current through both lamps in series, and noting the difference in candle-power.

In conclusion, two interesting qualities of Ta should be noted:—

The first is that when a Ta filament is heated in a high vacuum it will expel any oxygen that has combined with it. It is possible to detect whether a filament contains any oxide by very gradually heating it up, when the parts containing oxide will appear brighter than those consisting of pure Ta, owing to the greater electrical resistance of the oxide.

These lamps have been purposely exposed to the air while they were being exhausted and have become "spotty" in consequence, but if they are raised a little above their proper voltage and left burning for a few minutes, their filaments become quite uniform by the expulsion of the oxygen.

The second is that Ta will act as a rectifier when used in an electrolyte; that is to say, will allow of the passage of the positive current only in one direction. In the apparatus shown the positive current passes through the lamp to a Ta anode, thence to a Pt cathode, but in a very short time the Ta anode covers itself with a film of oxide which stops the current. When the current is reversed the lamp lights again and continues to burn. When an alternate current is connected to the lamp it will also continue to burn, but with reduced light.

All these experiments are intended to show the remarkable qualities of this material, and when they are fully appreciated and its limitations are properly understood, there appears to be a great field open to tantalum and its industrial applications.

THE ESTIMATION OF VANADIC AND ARSENIC ACIDS AND OF VANADIC AND ANTIMONIC ACIDS IN THE PRESENCE OF ONE ANOTHER.

By GRAHAM EDGAR.

Arsenic and Vanadium.

THE almost constant association of arsenic and vanadium in the mineral sources of both elements presents the frequent problem of their separation and estimation, and has led to the development of numerous analytical processes to accomplish the desired end. Carnot (*Comptes Rendus*, civ., 1803) precipitates all arsenic acid by boiling with a salt of strontium in weakly ammoniacal solution in the presence of ammonium salts. Gibbs (*Chem. Journ.*, vii., 230) precipitates the arsenic as trisulphide from a solution previously reduced with sulphur dioxide, the vanadium being determined in the filtrate by titration with potassium permanganate. Schmitz-Dumont (Inaug. Diss., Berlin, 1891) uses hydrogen sulphide under pressure to effect the separation. Friedheim and Michaelis (*Ber.*, xxviii., 1414), after reducing with sulphur dioxide the solution containing arsenic and vanadic acids, separate the former by repeated distillation with methyl alcohol and hydrochloric acid. Field and Smith (*Journ. Am. Chem. Soc.*, xviii., 1051) volatilise the arsenic by heating the dry sulphides of arsenic and vanadium in a current of hydrochloric acid gas at a temperature between 100° and 250° C. Friedheim, Decker, and Diem (*Zeit. Anal. Chem.*, xlv., 648) recommend the volatilisation of the arsenic by distillation with potassium iodide and hydrochloric acid, a current of hydrogen being kept up through the apparatus during the process.

In the present investigation any separation of arsenic and vanadium is avoided by the use of a process of differential reduction to determine these elements in the presence of one another.

TABLE I.

V ₂ O ₅ (grm.).			As ₂ O ₅ (grm.).			N/10 iodine (cc.).	
Taken.	Found.	Error.	Taken.	Found.	Error.	(I.).	(II.).
0.1183	0.1181	-0.0002	0.0960	0.0961	+0.0001	12.95	29.65
0.1183	0.1183	—	0.0960	0.0962	+0.0002	12.97	29.70
0.1183	0.1182	-0.0001	0.0960	0.0962	+0.0002	12.96	29.70
0.0591	0.0593	+0.0002	0.0480	0.0480	—	6.50	14.85
0.0591	0.0594	+0.0003	0.0480	0.0482	+0.0002	6.52	14.90
0.0591	0.0589	-0.0002	0.0480	0.0483	+0.0003	6.45	14.86
0.1774	0.1779	+0.0005	0.1440	0.1438	-0.0002	19.50	44.50
0.1774	0.1774	—	0.1440	0.1440	—	19.45	44.50
0.1774	0.1776	+0.0002	0.1440	0.1442	+0.0002	19.47	44.45
0.2366	0.2371	+0.0005	0.0480	0.0478	-0.0002	26.00	34.31
0.2366	0.2366	—	0.0480	0.0480	—	25.95	34.30
0.0591	0.0593	+0.0002	0.1440	0.1439	-0.0001	6.50	38.90

TABLE II.

V ₂ O ₅ (grm.).			Sb ₂ O ₅ (grm.).			N/10 × 0.9375 iodine (cc.).	
Taken.	Found.	Error.	Taken.	Found.	Error.	(I.).	(II.).
0.1183	0.1185	+0.0002	0.0757	0.0759	+0.0002	13.85	23.69
0.1183	0.1186	+0.0003	0.0757	0.0764	+0.0007	13.87	24.05
0.1183	0.1183	—	0.0757	0.0760	+0.0003	13.83	23.95
0.1774	0.1777	+0.0003	0.1261	0.1258	-0.0003	20.80	37.55
0.1774	0.1777	+0.0003	0.1261	0.1258	-0.0003	20.80	37.55
0.1774	0.1773	-0.0001	0.1261	0.1260	-0.0001	20.75	37.50
0.2366	0.2376	+0.0010	0.1261	0.1257	-0.0004	27.80	44.52
0.2366	0.2369	+0.0003	0.1261	0.1263	+0.0002	27.70	44.50
0.2366	0.2369	+0.0003	0.1261	0.1260	-0.0001	27.70	44.45

If a solution containing arsenic and vanadic acids is boiled with tartaric or oxalic acids, the vanadic acid is reduced to tetroxide and may be reoxidised in alkaline solution by iodine (Browning, *Zeit. Anorg. Chem.*, vii., 158; Browning and Goodman, *Am. Journ. Sci.*, ii., 355) according to the equation $V_2O_4 + I_2 + H_2O = V_2O_5 + 2HI$.

If a solution containing arsenic and vanadic acids is reduced with sulphur dioxide under proper conditions, the arsenic acid is reduced to arsenious acid and the vanadic acid to tetroxide, so that after boiling off the excess of reagent the reoxidation by iodine in alkaline solution should proceed according to the equation— $As_2O_3 + V_2O_4 + 3I_2 + 3H_2O = As_2O_5 + V_2O_5 + 6HI$, and the iodine thus used should correspond to the sum of the two oxides. If then aliquot parts of the same solution are treated in the manner described above, it is evident that the titration of the solution reduced by tartaric acid should determine the vanadium present, and that the titration of the solution reduced by sulphur dioxide should determine the sum of the arsenic and vanadium, the difference in the number of cubic centimetres of iodine used in the two cases being the amount required to oxidise the arsenic.

In Table I. are given the results of experiments performed upon solutions containing arsenic and vanadic acids in varying proportions. The method of treatment in detail was as follows:—The solutions were divided into two portions, and one of these was boiled with one to two grms. of tartaric or oxalic acid until the blue colour of the vanadium tetroxide indicated complete reduction. The solution was then cooled, nearly neutralised with potassium bicarbonate, and an excess of standard iodine solution was added. Neutralisation was then completed, an excess of bicarbonate added, and the solution allowed to stand for from fifteen minutes to one half hour. The excess of iodine was then removed with standard arsenious acid, and the solution titrated to colour after the addition of starch. The results of this titration are given under (I.), Table I.

The second portion of the solution was placed in a small pressure flask and slightly acidified with sulphuric acid. Twenty-five cubic centimetres of a strong solution of sulphurous acid was then added, and the flask was closed and heated for one hour on the steam-bath (McCay, *Am.*

Chem. Journ., vii., 273). After cooling, the flask was opened and the solution transferred to an Erlenmeyer flask and boiled to remove the excess of sulphur dioxide, a current of carbon dioxide being passed into the liquid to facilitate the removal of the last traces. The solution was then cooled, nearly neutralised with potassium bicarbonate, and an excess of iodine added as before. After completing the neutralisation, adding an excess of bicarbonate, and allowing to stand for one half hour, the excess of iodine was determined by arsenious acid as before. The results are given in (II.), Table I.

As before stated, the results in (I.) determine the vanadium, and these figures, subtracted from (II.), determine the arsenic.

Antimony and Vanadium.

Since antimonious acid is reduced by sulphur dioxide on heating in a pressure flask (Von Knorre, *Zeit. Angewandte Chem.*, 1888, clv.) there seemed no reason to suppose that antimony and vanadium should not be determined in the presence of each other by a process similar to the one used for arsenic and vanadium. Accordingly a series of experiments was made in which solutions containing vanadic acid and antimonious acid were treated in a manner exactly similar in detail to the preceding. The results are given in Table II.

Summary.

In a preceding paper it has been shown that vanadic and arsenic acids, or vanadic and antimonious acids, may be readily determined in the presence of one another by a method based upon the differential reducing action of tartaric or oxalic acid and sulphur dioxide, the re-oxidation being in each case effected with iodine in alkaline solution under the conditions described above.—*The American Journal of Science*, xxvii., April, 1909.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 1st inst., The Duke of Northumberland, K.G., President, in the Chair. Mr. James Douglas was elected a Member. The Special Thanks of the Members were returned to Sir William Farrer for his donation of £50 to the Fund for the Promotion of Experimental Research at Low Temperatures.

SOME FORMS OF FOOD ADULTERATION AND SIMPLE METHODS FOR THEIR DETECTION.*

By W. D. BIGELOW Chief of the Division of Foods,
and
BURTON J. HOWARD, Chief of the Microchemical Laboratory.
(Continued from p. 218).

Fruit Products.

THE class of goods known as fruit products includes jams, jellies, marmalades, and dried and preserved fruits of every description. Glucose is often used as a substitute for cane-sugar, and colouring matter is employed in order that the colour of the finished article may stand for a considerable time on the shelves in the light without deterioration. Colouring matter is also used with cheap fruits in the preparation of a product supposedly made from more expensive products. For instance, jellies are sometimes made of glucose and apple juice, the latter having been prepared from peelings and cores, the by-product of the manufacture of dried apples. These jellies may be flavoured and coloured to represent the jelly of high priced fruits, or they may be sold without additional flavour and as a low priced product. Always, however, when the product of a high priced fruit is imitated artificial colouring matter is employed.

Apple juice, as mentioned above, and especially the product obtained from peelings and cores, is used extensively with the cheaper grades of jellies where but little fruit is used. With the cheapest grade of goods, starch is often used as a filler and gelatinising agent.

Preservatives, such as salicylic acid and benzoic acid, are often employed with jellies and jams. Their purpose is twofold:—First, to preserve apple juice in barrels until it is desired in the manufacture of the finished product; second, to prevent moulding in the finished article which is subjected to much less favourable conditions during transportation on trains and in heated storerooms than is the case of the domestic product, which stands quietly, often in a cool, dark cellar, from the time it is made until it is used.

The exhausted apple residue from the manufacture of jelly is sometimes used for the preparation of jams, giving to the latter the seeds and other insoluble material of the fruit supposed to be present, while the soluble material is frequently made up of glucose. Occasionally foreign seeds are used for this purpose. Glucose, as has been already stated, is commonly used in the cheaper varieties of fruit products, and sometimes, though very rarely, saccharin is employed for sweetening.

Meat Preparations.

In this class of foods are considered fresh and prepared meat, fish, crabs, oysters, and similar products. The fresh meats on the market are rarely subject to adulteration. Packers depend entirely on cold storage for their preservation, and they are kept at a low temperature, not only in the packing-house, but also in refrigerator cars in transit and in cold storage rooms at their destination until immediately before they go into consumption.

In fresh meats, however, preservatives are sometimes employed by retail dealers who have not efficient refrigerator service or who desire to keep fresh meat for a considerable time on the block. For this purpose powdered preparations of preservatives are employed, and dusted over the meat from time to time.

All varieties of meat that are sold in a finely comminuted state, such as chopped meat, Hamburg steak, and sausage, are likely to have a preservative added in their preparation. By this statement it is not meant that preservatives are added in all cases. Their use, however, simplifies the keeping of such preparations and is not unusual. The preservatives most commonly employed with meat are

borax or boric acid and sulphites. Oysters, when kept in bulk after shucking, are also frequently preserved.

It is frequently pointed out by manufacturers that the addition of preservatives does not restore the fresh character of spoiled meat, and that they can not be used for this purpose. As has been stated above, however, sometimes meat, especially in a finely comminuted condition, frequently loses its natural fresh colour before there is any other evidence of deterioration. This colour is restored to a certain extent by the addition of sulphites, and the colour is very materially preserved if sulphites are added at the time of the preparation of chopped meat. Moreover, manufacturers of chemical preservatives frequently add a small amount of coal-tar colour to preservatives consisting of sulphites intended to be added to meat.

One of the most objectionable forms of adulteration practised in connection with meat is the sale of the flesh of immature calves. This practice is forbidden in practically all of the States, but the enforcement of such laws has sometimes been found very difficult. Particular difficulty has been experienced in this matter in New York.

Spices.

Spices offer many opportunities for the food adulterator. They are usually sold after being ground, and for that reason are easily imitated. Practically all varieties of ground spices are adulterated by some grinders and in some markets. The products ordinarily used for the purpose of adulterating spices are cereals and cereal products (such as ground wheat and Indian corn), ground shells of cocoa-nuts, almond shells (sometimes parched), olive pits, and sawdust. The cheaper varieties of spices are sometimes substituted for the more valuable kinds, and stems, husks, &c., may be added. These adulterants are mainly objectionable because of the fraud connected with their use.

Products are made in imitation of the various spices and sold for three and a-half or five cents a pound to mixers and others who use them in the preparation of low-grade goods, while the products that they imitate are worth from sixteen to sixty cents a pound. These articles have the physical appearance of the spices they are intended to represent, but are entirely without any spice flavour. They are sometimes coloured with coal-tar derivatives or other colouring matter, for the purpose of more nearly simulating the spices they are intended to imitate.

Colours, stems, and cocoa-nut shells are imported into the United States in considerable quantity for the purpose of adulterating spices. Bombay mace and wild mace are products belonging to the same class of plant products as true mace, and bear a general resemblance to it, but they have very little flavouring power, and hence constitute an adulteration when mixed with it.

Sugars, Syrups, &c.

As a class the sugars, both high and low grades, as found on the market are practically free from adulteration. During recent years, however, a product has been put on the market to a limited extent which consists of a mixture of cane-sugar with starch sugar (glucose) and saccharin, the latter being an artificial sweetening material derived from coal-tar. There is a popular belief that granulated sugar is often adulterated with white sand or pulverised rock, and that pulverised sugar is commonly adulterated with starch or lime dust. Cases of such adulteration, however, have never been found by this Bureau, and it may safely be said that they occur rarely if at all.

Considering the obvious simplicity of a method of determining the presence of such a substance, it is strange that the idea that material of this nature commonly occurs in sugar should be as prevalent as it is. Sugar is readily soluble in water, and sand and mineral substances insoluble. If a spoonful of sugar be placed in a glass of water, therefore, and the mixture stirred, solution will be complete. The substances mentioned above, if present, would remain undissolved. Of course solution will occur more readily if

* Bulletin No. 109, Bureau of Chemistry, U.S. Department of Agriculture.

the water is warm, and care must be taken to continue the mixing for a considerable time. A sample of granulated or powdered sugar suspected of being adulterated with sand or pulverised rock may, therefore, be readily examined by anyone who is interested.

Vinegar.

Vinegar in the United States is understood to be the product of the acetic fermentation of apple juice without any other addition whatever. In France vinegar is understood to be the product of the acetic fermentation of wine.

Several other classes of vinegar are made in considerable amount. Malt vinegar prepared by the acetic fermentation of an infusion of malt, is made in large quantities in the United States and in England. Large quantities of distilled vinegar are made by the acetic fermentation of alcohol. This product is made in considerable quantity by distilleries, and is frequently sold incorrectly as white wine vinegar.

The chief frauds practised in the sale of vinegar are, first, the dilution of cider vinegar and wine vinegar; second, the adulteration of those vinegars with vinegars of the cheaper sorts, such as distilled vinegar; third, the sale of distilled vinegar as cider vinegar or wine vinegar, with or without the addition of colouring matter and other substances to make it resemble those products.

(To be continued).

A REVISION OF THE ATOMIC WEIGHT OF CHROMIUM.*

SECOND PAPER.—THE ANALYSIS OF SILVER DICHROMATE.

By GREGORY PAUL BAXTER
and
RICHARD HENRY JESSE, Jun.

(Concluded from p. 216).

The Specific Gravity of Silver Dichromate.—The specific gravity of silver dichromate has been found by Schroeder to be 4.669 (*Liebig's Jahresb.*, 1879, p. 31), but on account of the uncertainty of most of the older specific gravity determinations, this constant was very kindly re-determined for us by Mr. Victor Cobb. The silver dichromate was precipitated from dilute nitric acid solution, and once re-crystallised from normal nitric acid. Then it was dried at 200° for many hours. The determination was effected by displacement of toluene of specific gravity 0.86218. Care was taken to extract entangled air from the crystals by exhausting the air from the pycnometer in a vacuum desiccator.

Weight of $\text{Ag}_2\text{Cr}_2\text{O}_7$ in vacuum.	Weight of toluene displaced in vacuum.	Specific gravity of $\text{Ag}_2\text{Cr}_2\text{O}_7$.
Grms.	Grms.	25°/4.
29.308	5.299	4.769
25.330	4.578	4.770

The following corrections were applied:—

	Specific gravity.	Vacuum correction.
Weights	8.3	—
Toluene	0.862	+0.00126
Silver dichromate ..	4.770	+0.000107
Silver bromide	6.473	+0.000041
Silver chloride	5.56	+0.000071

A No. 10 Troemner balance easily sensitive to one-fiftieth of a mgrm. was used in all the weighings. The gold-plated weights were carefully standardised to hundredths of a mgrm. by the method described by Richards (*Journ. Am. Chem. Soc.*, 1900, xxii., 144).

Weighing was always carried out by substitution, with

the use of a counterpoise as nearly as possible like the object weighed, both in material, shape, and volume.

The accompanying table gives the results of all the final experiments in the order in which they were carried out. The preliminary analyses, which were defective in various ways, are not recorded.

The results of the foregoing experiments are as concordant as one can reasonably expect, since the insoluble silver salts are, in general, difficult to obtain definite in composition (Baxter and Coffin, *Journ. Am. Chem. Soc.*, 1909, xxxi., 247; Baxter, Mueller, and Hines, see former article). The extreme values differ by only one one-hundredth of a per cent, while the averages of the different samples show an extreme difference of less than five-thousandths of a per cent. The composition of the dichromate is evidently not affected by the concentration of the nitric acid from which it is crystallised, since the averages from the different samples do not vary regularly with the concentration of the nitric acid, the average result obtained from Sample II. being lower than that of either Sample I. or Sample III.

If the per cent of silver in silver dichromate is 49.9692, the molecular weight of silver chromate may be calculated from the atomic weight of silver, and from the molecular weight of the chromate the atomic weight of chromium by difference. Since the ratio of the atomic weights of silver and oxygen is somewhat uncertain at the present time, these calculations have been made with various possible assumed values for the atomic weight of silver, oxygen being assumed to have the value 16.000. It is to be noted that the percentage error in the determination of the molecular weight of silver chromate is multiplied four times in the atomic weight of chromium.

If Ag = 107.930	$\text{Ag}_2\text{Cr}_2\text{O}_7 = 431.986$	and Cr = 52.063
If Ag = 107.880	$\text{Ag}_2\text{Cr}_2\text{O}_7 = 431.786$	and Cr = 52.013
If Ag = 107.850	$\text{Ag}_2\text{Cr}_2\text{O}_7 = 431.666$	and Cr = 51.983

In the following table are given the results of the former research upon silver chromate by Baxter, Mueller, and Hines, together with the average of their values and those presented in this paper:—

	Baxter, Mueller, and Hines.	Average.
If Ag = 107.930	Cr = 52.062	52.063
If Ag = 107.880	Cr = 52.008	52.011
If Ag = 107.850	Cr = 51.976	51.980

The agreement of the two independently determined values is highly satisfactory, no matter which value for the atomic weight of silver is assumed, although the higher values for silver give slightly better agreement.

The atomic weights of both chromium and silver may be calculated independently of any assumption except the atomic weight of oxygen from the following equations:—

$$2\text{Ag}/(2\text{Ag} + \text{Cr} + 64) = 0.650333$$

$$2\text{Ag}/(2\text{Ag} + 2\text{Cr} + 112) = 0.499692$$

to be 52.074 and 107.941 respectively. However interesting these results may be, they have little real significance, since an error of five-thousandths of a per cent in either ratio causes an error of over one-tenth of a unit in the atomic weights of both silver and chromium.

The most important results of this research are as follows:

1. Pure silver dichromate was prepared.
2. It is shown that silver dichromate cannot be completely dried without decomposition.
3. It is shown that silver dichromate when crystallised from nitric acid retains traces of the nitric acid.
4. The proportion of moisture and nitric acid in silver dichromate treated in definite fashions was determined.
5. The specific gravity of silver dichromate is found to be 4.770 at 25° referred to water at 4°.
6. The per cent of silver in silver dichromate is found to be 49.9692.

* Contributions from the Chemical Laboratory of Harvard College. From the *Journal of the American Chemical Society*, xxxi., No. 5.

SERIES III.—2AgBr : Ag₂Cr₂O₇.

Ag/AgBr = 0.574453 (Baxter, *Journ. Am. Chem. Soc.*, 1906, xxviii., 1322).

No. of analysis.	Sample of Ag ₂ Cr ₂ O ₇ .	Corrected weight of Ag ₂ Cr ₂ O ₇ in vacuum.	Weight of AgBr in vacuum.	Weight of asbestos.	Dissolved AgBr from filtrate.	Loss on fusion.	Corrected weight of AgBr in vacuum.	Ratio, 2AgBr : Ag ₂ Cr ₂ O ₇
		Grms.	Grms.	Grm.	Grm.	Grm.	Grms.	
1.	II.	5.71554	4.97107	0.00024	0.00025	0.00007	4.97149	0.869820
2.	II.	4.87301	4.23870	0.00019	0.00003	0.00004	4.23888	0.869869
3.	II.	7.45476	6.48380	0.00034	0.00019	0.00008	6.48425	0.869813
4.	III.	4.75269	4.13409	0.00020	0.00003	0.00012	4.13420	0.869865
5.	III.	8.15615	7.09477	0.00022	0.00005	0.00009	7.09495	0.869890
6.	III.	6.15412	5.35306	0.00007	0.00007	0.00011	5.35309	0.869839
7.	I.	6.83662	5.94656	0.00030	0.00009	0.00017	5.94678	0.869842
8.	I.	5.39883	4.69610	0.00027	0.00007	0.00013	4.69631	0.869876
9.	III.	6.26657	4.16034 (a)	0.00018	0.00040	0.00016	4.16076	0.869903 (b)
Average								0.869857
Total								48.37126
Average from Sample I.								0.869854
" " II.								0.869859
" " III.								0.869874
Average								0.869856

Per cent of Ag in Ag₂Cr₂O₇ if 2AgBr : Ag₂Cr₂O₇ = 0.869857 : 1.000000 49.9692

(a) AgCl.

(b) Calculated from the ratio AgBr : AgCl = 131.0171 : 100.0000. Baxter (*loc. cit.*), 4.16076 grms. AgCl = 5.45131 grms. AgBr.

7. With several assumed values for the atomic weight of silver referred to oxygen 16.000, the atomic weight of chromium is found to have the following values :—

If Ag = 107.93	Cr = 52.06
If Ag = 107.88	Cr = 52.01
If Ag = 107.85	Cr = 51.98

8. If these results are averaged with those previously found by Baxter, Mueller, and Hines, the atomic weight of chromium is found to be as follows :—

If Ag = 107.93	Cr = 52.06
If Ag = 107.88	Cr = 52.01
If Ag = 107.85	Cr = 51.98

We are greatly indebted to the Carnegie Institution at Washington for generous pecuniary assistance in pursuing this investigation; also to the Cyrus M. Warren Fund for Research in Harvard University for many pieces of platinum apparatus.

Royal Institution.—The 84th Christmas Course of Juvenile Lectures, founded at the Royal Institution in 1826 by Michael Faraday, will be delivered this year by Mr. William Duddell, F.R.S., his subject being "Modern Electricity." The Course, which will be experimentally illustrated, commences on Tuesday, December 28, at 3 o'clock, and will be continued on December 30, 1909, January 1, 4, 6, and 8, 1910.

Association of Teachers in Technical Institutions.—The Annual Meeting of this Association will be held on November 6th, at St. Bride Institute, Fleet Street, E.C. The Chair will be taken at 3 p.m. by Mr. J. Wilson, who is to be President of the Association for the coming year. One of the principal items of business of this meeting will be the consideration of the Annual Report of the Council. This Report will contain an abstract of the educational and professional work accomplished during the year. The educational work comprises the consideration of such questions as syllabuses in such subjects as Applied Mechanics and Electrical Engineering, the Training of Craftsmen, the Preliminary Training of Technical Students, and the Royal Commission on University and Higher Education in London. Amongst professional matters dealt with are registration of teachers, superannuation, legal matters, and a minimum scale of salaries for teachers in technical institutes.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

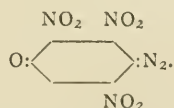
THE following are abstracts of papers received during the vacation and published or passed for publication in the *Transactions* :—

188. "The Action of Bromocyclohexane and of 4-Bromo-1-methylcyclohexane on the Sodium Derivative of Ethyl Malonate." By EDWARD HOPE and W. H. PERKIN, jun. (*Trans.*, 1909, 1360).

The authors have prepared ethyl cyclohexylmalonate and ethyl 1-methylcyclohexyl-4-malonate by the above reactions; the properties of these substances and their derivatives are described.

189. "2 : 3 : 5-Trinitro-4-aminophenol and Derivatives." By RAPHAEL MELDOLA and JAMES GORDON HAY (*Trans.*, 1909, 1378).

This compound has been isolated by the careful hydrolysis of the acetyl derivative by means of sulphuric acid. It crystallises from acetic acid in deep red needles decomposing at about 145°. The most important conclusion deduced from the study of the substance is that the loss of a nitro-group on diazotisation is primarily due to the mobility conferred by the presence of a methoxy-group, since the present compound, although highly nitrated and possessing a nitro-group in a most favourable position for elimination, can be diazotised with the retention of all its nitro-groups, the diazonium sulphate passing at once on dilution with water into 2 : 3 : 5-trinitroquinonediazide :—



The 3-nitro-group of this compound is capable of being replaced by hydroxy- and alkoxy-groups without the removal of the diazo-group.

190. "Colour and Constitution of Azo-compounds." Part IV. By JOHN THEODORE HEWITT and FERDINAND BERNARD THOLE (*Trans.*, 1909, 1393).

In order to obtain more insight into the relationship between constitution and selective absorption, the following bisazo-compounds of relatively simple type have been prepared and examined.

Benzeneazobenzeneazodimethylaniline, m. p. 190° (uncorr.), and its hydrochloride, C₂₀H₁₉N₅, HCl; *o*-tolueneazo-*o*-tolueneazodimethylaniline, m. p. 138° (uncorr.), and its hydrochloride, C₂₂H₂₃N₅, HCl; benzeneazobenzeneazophenol, m. p. 180° (uncorr.); benzeneazobenzeneazophenyl acetate, m. p. 178° (uncorr.).

The absorption of these substances in acid solutions has been examined for the visible part of the spectrum. The dimethyl-amino-compounds dissolve in concentrated sulphuric acid with a red colour, passing to blue on dilution; the blue solutions correspond with the salts of a mono-acid base. The phenolic compound dissolves in concentrated sulphuric acid with a fine purple colour, dilution producing complete hydrolysis.

191. "*The Amygdalins.*" Part I. By J. WALLACE WALKER and VERNON K. KRIEBLE. (*Trans.*, 1909, 1437).

The study of the action of traces of alkali on *l*-amygdalin, first observed by one of the authors (Walker, *Trans.*, 1903, lxxxiii., 472), has been continued, and a partial resolution of the racemised solution has been effected. The equilibrium between the different varieties has been found to be unaffected by changes in the concentration and nature of the alkali, or in the concentration of the amygdalin, or by temperature. The great difference in the action of emulsin on the several modifications shows, however, that a further change takes place in the racemised solution on heating, and renders it doubtful whether the crystalline material separated from the racemised solution contains *d*-amygdalin or an isomeric substance.

192. "*The Action of the Grignard Reagent on Phthalic Esters.* By YUJI SHIBATA. (Trans., 1909, 1449).

The author has studied the action of the Grignard reagent on phthalic esters, and finds that, in spite of the close analogy of phthalic acid to succinic acid, the action of the Grignard reagent on phthalic esters differs from that on succinic esters in producing derivatives of phthalide, instead of glycols. More frequently, the reaction proceeds one step further, with the production of derivatives of phthalane. 1:1-Dimethyl-3-methylenephthalane, 1:1-diphenyl-3-phenylenephthalane, and 1:1-dibenzyl-3-benzylidenephthalane have thus been obtained. Of the various space formulæ proposed for benzene from time to time, that of Gracbe, which represents Kekulé's well known formula in space, accounts most satisfactorily for the results obtained in this investigation.

193. "Constitution of Hydroxyazo-compounds. Part II. Action of Mercuric Acetate on Benzeneazobiphenols." By ALEC DUNCAN MITCHELL and CLARENCE SMITH. (*Trans.*, 1909, 1430).

In continuation of former work (*Trans.*, 1908, xciii., 842), the action of mercuric acetate on hydroxyazo-compounds of the naphthalene series in alcohol has been examined. Benzeneazo- β -naphthol does not react with the salt, whilst benzeneazo- α -naphthol undergoes oxidation to Witt and Dedichen's $\beta\beta$ -dinaphthyl derivative (*Bcr.*, 1897, xxx., 2660). When the β -position contains a substituent, the oxidation is prevented and monomeric acetates are formed.

β-Benzeneazo-α-naphthol mercuriacetate,

$$\text{C}_6\text{H}_5 \cdot \text{N}_2 \cdot \text{C}_{10}\text{H}_5(\text{OH}) \cdot \text{Hg} \cdot \text{CO}_2 \cdot \text{CH}_3,$$

m. p. 208° (decomp.), is a red powder sparingly soluble in the usual solvents, except glacial acetic acid; by prolonged boiling with the latter, the mercuriacetate group is replaced by hydrogen. 4-Nitro-2-benzeneazo- α -naphthol mercuriacetate, $C_6H_5N_2C_{10}H_7(OH)(NO_2) \cdot Hg \cdot CO_2 \cdot CH_3$, m. p. 221—222°, is a dull red powder obtained from 4-nitro-2-benzeneazo- α -naphthol, m. p. 178—179°, which crystallises in dark red needles and forms an acetate, m. p. 208°, crystallising in orange-yellow needles. 2-Nitro-4-benzeneazo- α -naphthol mercuriacetate is a lustrous, reddish brown substance, which blackens on heating, but does not melt below 200°; it is obtained from 2-nitro-4-benzeneazo- α -

naphthol, m. p. 164° , which crystallises in orange-red needles, and forms an *acetate*, m. p. 173 , crystallising in red prisms. *Bisbenzenazo-a-naphthol mercuriacetate*, $(C_6H_5 \cdot N_2)_2C_{10}H_4(OH) \cdot Hg \cdot CO_2 \cdot CH_3$, m. p. $235-239^{\circ}$ (decomp.), separates from phenol generally as a dark purplish-brown mass, but on one occasion was obtained in black bronzy needles. *2':4':6'-Tribromo-2-nitro-4-benzenazo-a-naphthol*, m. p. 216° , orange-yellow plates, *2':4':6'-tribromo-4-nitro-2-benzenazo-a-naphthol*, m. p. $215-216^{\circ}$, orange-red needles, and *bis-2':4':6'-tribromobenzenazo-a-naphthol*, m. p. $249-253^{\circ}$, a maroon powder, have also been prepared.

194. "*Preparation of the Acyl Derivatives of the Aldehycyanohydrins.*" Part I. By FRANCIS FRANCIS and OLIVER CHARLES MINTY DAVIS. (*Trans.*, 1900, 1403).

It has been found that aromatic aldehydes readily react with acid chlorides in the presence of aqueous potassium cyanide to form the acyl derivatives of the corresponding cyanohydrins. The reaction may be generalised and expressed as follows:—

$$R \cdot CHO + R' \cdot COCl + KCN \rightarrow R \cdot CH(O \cdot COR') \cdot CN + KCl.$$

195. "The Action of Phosphorus Pentachloride on the Methylene Ethers of Catcchl Derivatives. Part V. Derivatives of Protocatechuyl Alcohol and Protocatechuonitrile." By ARTHUR JAMES EWINS. (*Trans.*, 1909, 1482).

No dichloromethylene derivative can be isolated by the direct action of phosphorus pentachloride on piperonyl alcohol (Barger, *Trans.*, 1908, xciii., 567); the corresponding chloride, $\text{CH}_2\text{:O}_2\text{:C}_6\text{H}_3\text{:CH}_2\text{Cl}$ (Decker and Koch, *Ber.*, 1905, xxxviii., 1739), however, readily yields 3:4-dichloromethylenedioxibenzyl chloride, $\text{CCl}_2\text{:O}_2\text{:C}_6\text{H}_3\text{:CH}_2\text{Cl}$, b. p. 154–156°/16 mm., which is transformed by formic acid into 3:4-carbonyldioxibenzyl chloride, $\text{CO:O}_2\text{:C}_6\text{H}_3\text{:CH}_2\text{Cl}$, m. p. 57° (compare Pauly and Alexander, *Ber.*, 1909, xlii., 2350). By boiling 3:4-carbonyldioxibenzyl chloride with water, an impure crystalline catechol derivative free from chlorine was obtained (protocatechuyl alcohol?).

By a similar series of reactions, piperonylnitrile yields successively 3 : 4-dichloromethylenedioxybenzonitrile, $\text{CCl}_2\text{:O}_2\text{:C}_6\text{H}_3\text{:CN}$, b. p. $155-156^\circ/15\text{ mm.}$, m. p. $76-77^\circ$; 3 : 4-carbonyldioxybenzonitrile, $\text{CO:O:C}_6\text{H}_3\text{:CN}$, prisms from benzene, m. p. 112° , and 3 : 4-dihydroxybenzonitrile (protocatechuonitrile), $\text{C}_6\text{H}_3(\text{OH})_2\text{:CN}$, needles from water, m. p. 152° .

By the action of phosphorus pentachloride on 3:4-methylenedioxy mandelamide, $\text{CH}_2:\text{O}_2:\text{C}_6\text{H}_3\text{CH}(\text{OH})\cdot\text{CO}\cdot\text{NH}_2$ (Barger and Ewins, *Trans.*, 1909, xcv., 555), and boiling the product with formic acid, 3:4-methylenedioxyphenylglyoxylonitrile, $\text{CH}_2:\text{O}_2:\text{C}_6\text{H}_3\cdot\text{CO}\cdot\text{CN}$, was obtained.

The abnormal reaction between piperonyl alcohol and phosphorus pentachloride is due to the condensation, under the influence of phosphorus halides, of the piperonyl chloride first produced to a substance, $C_{16}H_{12}O_4$, m. p. 360° , which sublimes under diminished pressure, and is probably related to anthracene. Its formation may be expressed by the equation:—

$$2\text{CH}_2:\text{O}_2:\text{C}_6\text{H}_3\cdot\text{CH}_2\text{Cl} =$$

$$= \text{CH}_2:\text{O}_2:\text{C}_6\text{H}_2\langle\text{CH}_2\rangle\text{C}_6\text{H}_2:\text{O}_2:\text{CH}_2 + 2\text{HCl}.$$

A crystalline *nitro*-derivative of the probable composition $C_{16}H_{10}O_4(NO_2)_2$ was obtained.

196. "*The Preparation of Disulphides. Part VI. Note on a New Method of Preparing Disulphides.*" By THOMAS SLATER PRICE and DOUGLAS FRANK TWISS. (*Trans.*, 1909, 1489).

Although alkyl thiosulphates do not react with iodine at the ordinary temperature, reaction readily takes place at higher temperatures, the corresponding disulphides being formed according to the equation:— $2\text{KO}\cdot\text{SO}_2\text{SR} + 2\text{H}_2\text{O} + \text{I}_2 = \text{R}_2\text{S}_2 + 2\text{KHSO}_4 + 2\text{HI}$. The yield of disulphide is practically quantitative. The preparation of benzyl disulphide, *o*-nitrobenzyl disulphide, and dimethyl dithiodiglycolate is described.

197. "Halogen Derivatives of Cinnamic Acid." By THOMAS CAMPBELL JAMES and JOHN JOSEPH SUDBOROUGH. (*Trans.*, 1909, 1538).

Further experiments have been made on the addition of bromine to methyl and ethyl cinnamate.

The action of alkalis on *d*- and *l*-cinnamic acid dibromides and on methyl and ethyl allocinnamate dibromides has been studied, and also the action of various organic bases on cinnamic acid dibromide.

Attempts have been made to resolve α -bromo- and α -bromo-allocinnamic acids into optically active components, but without success.

198. "The Conversion of Pinene into Sobrerol." By GEORGE GERALD HENDERSON and WILFRED JAMES STEVENSON EASTBURN. (*Trans.*, 1909, 1465).

Not only the mixture of *d*- and *l*-pinene obtained from American oil of turpentine, but also *d*-pinene and *l*-pinene themselves, yield the inactive modification of sobrerol when oxidised with aqueous mercuric acetate by the method formerly described, and therefore optical inversion occurs in the process.

Using the formation of sobrerol as a test, the presence of *d*-pinene in a specimen of Russian oil of turpentine has been proved, whilst a sample of Swedish oil of turpentine gave a negative result.

199. "Influence of various Sodium Salts on the Solubility of Sparingly Soluble Acids." (Part II.). By JAMES CHARLES PHILIP and FREDERICK BASIL GARNER. (*Trans.*, 1909, 1466).

The work described in an earlier paper (*Trans.*, 1905, lxxxvii, 987) has been extended. In harmony with what was then found, the authors find that the weaker the acid from which the sodium salt is derived, the greater is the influence of the salt on the solubility of benzoic, salicylic, *o*-chlorobenzoic, and *m*-nitrobenzoic acids. It is further found that if of two sparingly soluble acids the weaker is also the more soluble, then under the influence of any sodium salt the solubility of the stronger acid is increased to a greater extent than that of the other. The experimental figures for the solubility are compared with those calculated by Noyes's formula, and the agreement between the two sets of values is generally good.

200. "Organic Derivatives of Arsenic. Part II. Triaminotriphenylarsine Oxide and Tricamphorylarsinic Acid." By GILBERT T. MORGAN and FRANCES M. G. MICKLETHWAIT. (*Trans.*, 1909, 1473).

Triaminotriphenylarsine oxide, $O:As(C_6H_5)_3 \cdot NH_2)_3$, was produced by condensing aniline and arsenious chloride in boiling benzene or toluene, and treating the mixture with aqueous alkali.

Tricamphorylarsinic acid, $(C_{10}H_{15})_3As(OH)_2$, was isolated from the products of the interaction of sodium camphor and arsenious chloride.

201. "The Estimation of Arsenic in Organic Compounds." By HARRY F. V. LITTLE, EDWARD CAHEN, and GILBERT T. MORGAN. (*Trans.*, 1909, 1477).

The compounds were heated with sodium peroxide and sodium carbonate, the acidified aqueous extract of the fusion boiled with potassium iodide, and the arsenic precipitated as sulphide. The precipitate was re-dissolved in aqueous sodium hydroxide, and the solution treated with hydrogen peroxide. After acidifying and boiling to decompose the excess of peroxide, the reduction with potassium iodide was repeated, the liberated iodine boiled off, and the resulting arsenious solution neutralised and titrated with standard iodine solution.

202. "A Method of Harmonising the Atomic Weights." By JAMES MOIR.

The author assumes the cause of valency to be the presence, in varying numbers, of a sub-element of atomic weight $1/112$, and regards the main bulk of the mass of the elements as due to polymerisation of an entity consisting of the hydrogen atom, less the above aggregation; thus, if the fraction $1/112$ be represented by μ , a

bivalent element contains 2μ , and denoting the entity referred to by $\bar{H}$, the atomic weight of oxygen, for example, $= 16\bar{H} + 2$. By the application of this idea, close agreement is found between the calculated and observed values for the atomic weights of the elements.

203. "The Spontaneous Crystallisation of Solutions of Sodium Carbonate and Sodium Thiosulphate." By BERNARD MOUT JONES. (*Trans.*, 1909, 1672).

The author has determined the conditions under which spontaneous crystallisation takes place in the systems sodium carbonate-water and sodium thiosulphate-water when solutions of these salts, freed from crystal nuclei, are slowly cooled (or warmed) with constant shaking in the presence of glass fragments. In the first system, solutions of concentration of from 5 to 48 parts of anhydrous salt to 100 parts of water, on cooling and shaking, give crystals of ice or decahydrate at definite temperatures. These give rise to well-defined supersolubility curves intersecting in a "hypertectic" point at -7.6° , and running roughly parallel to the corresponding solubility curves.

The solubility of the monohydrate has a negative temperature-coefficient, and saturated solutions therefore have to be warmed in order to bring about crystallisation of this salt. A supersolubility curve for this phase has been traced. At higher temperatures it becomes practically coincident with the solubility curve, since the latter is almost parallel to the temperature axis.

Of the fourteen possible solid phases which may separate out from solutions of sodium thiosulphate, only two, ice and the secondary monohydrate, give rise to definite supersolubility curves. When dilute solutions of concentrations between 0 and 40 parts anhydrous salt to 100 parts of water are slowly cooled and shaken, ice separates out at definite temperatures. With concentrated solutions under concentrations of 179 and 255, under the same conditions, the secondary monohydrate always appears at definite temperatures.

The spontaneous crystallisation of anhydrous salt, primary dihydrate, and primary and secondary pentahydrates has been observed in solutions kept at rest for long periods.

204. "The Effect of Contiguous Unsaturated Groups on Optical Activity. Part II. Acids containing two Adjacent Ethenoid Groups." By THOMAS PERCY HILDITCH. (*Trans.*, 1909, 1570).

An effort has been made to determine the effect of two conjugated ethylenic bands on the optical activity of an organic compound by means of the study of active esters and salts of acids containing this system, together with their reduction products. Derivatives of muconic, sorbic, piperic, cinnamylidenemalononic, and the corresponding $\alpha\beta$ - and $\beta\gamma$ -dihydro- and tetrahydro-acids have been examined in this way, with the following results:—

1. In all cases the compound possessing two contiguous ethenoid linkings shows a very marked optical exaltation with respect to either the monoethylenic or the fully saturated acids.

2. As previously observed in other instances, the monoethylenic derivatives possess greater rotatory power than the saturated compounds, but the anomaly is of a much smaller order than that due to the conjugated system.

3. The phenyl group in the δ -position with respect to carboxyl appears to exert a depressing influence on optical rotatory power.

4. Adipic acid, although fully saturated, shows distinct exaltation of rotatory power in its optically active esters and salts.

5. Muconic acid derivatives, possessing a structure symmetrical with respect to the centre of the conjugated system, show the most enhanced anomaly of all.

205. "The effect of Contiguous Unsaturated Groups on Optical Activity. Part III. The Normal Series of Fatty Dibasic Acids." By THOMAS PERCY HILDITCH. (*Trans.*, 1909, 1578).

The dimethyl esters and dibrucine salts of the acids from oxalic to sebacic inclusive have been prepared and examined polarimetrically in chloroform solution.

The oxalic derivatives show a very pronounced exaltation of optical activity; the malonic and succinic compounds show a depression below the normal value, similar to that previously noted in the case of formic and acetic acid compounds; and, finally, adipic acid shows a distinct exaltation, although not so great as in oxalic acid. The glutaric compounds and derivatives of the higher acids are all approximately normal.

It is suggested that, whilst the anomaly in the case of oxalic acid is obviously due to the contiguity of two carboxyl groups, the cause of the enhanced values of dimethyl and dibrucine adipates may be the contiguity of the carboxyl groups in space, which, according to the usually accepted stereochemical views, would occur in adipic acid and its derivatives.

(To be continued).

NOTICES OF BOOKS.

Quantitative Chemical Analysis. By FRANK CLOWES, D.Sc., Lond., and J. BERNARD COLEMAN, A.R.C.Sc., Dublin. Eighth Edition. London: J. and A. Churchill. 1909.

FRESH editions of this well-known and widely used treatise on Quantitative Analysis, which is intended for use in the laboratories belonging to schools and colleges, follow on one another with great rapidity, and in each one some improvements are to be found. The eighth edition contains considerably more matter than the preceding, and the size of the page has been increased accordingly. Some new volumetric and electrolytic methods are described in it, and a section dealing with the examination of oils, fats, and waxes has been added. The only criticism that can be offered on such an excellent treatise is that some details relating to the analysis of cereals might have been added with advantage, for it affords good practice in simple quantitative work and is a process of great importance.

Catechism Series. Chemistry. Part II. Inorganic and Organic. Edinburgh: E. and S. Livingstone.

THIS short catechism on chemistry will be found useful by examination candidates, for it will serve to freshen their memory of some of the more important facts which they have learnt either from their reading of text-books or by their experimental work in the laboratory. It includes some of the metals and common organic substances, and in the form of question and answer recapitulates methods of preparation and the properties and reactions of a considerable number of compounds. Accuracy and succinctness are all that are required in a book of this kind, and the "Catechism" does not appear to fail in either respect.

The Lead and Zinc Pigments. By CLIFFORD DYER HOLLEY, M.S., Ph.D. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1909.

THIS book on the manufacture, uses, and analysis of the lead and zinc pigments deals almost exclusively with American practice, alluding to that of other nations only for the sake of comparison. The rapid growth of the pigment industry, and of the application of scientific principles to its consideration, especially in America, is demanding much commentative and summarising literature, and of such books the one now under review is a favourable specimen. The author possesses a wide knowledge of the practical details of the manufacture of pigments, and as Chief Chemist to the Acme White Lead and Colour Works he has had unique opportunities, of which he has made the fullest possible use, of acquiring information on the subject. He lays great stress upon practical aspects, and gives

details of tests which have been carried out to determine the values and most suitable methods of using different pigments, displaying no bias in favour of any particular brand, and for the most part leaving the reader to form his own conclusions. The book includes short descriptions of methods of determining both the qualitative and quantitative composition of pigments.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlviii., No. 11, September 13, 1909.

Determination of Phosphorus in Combustible Substances by means of the Calorimetric Bomb.—P. Lemoult.—The calorimetric bomb can be employed for the determination of phosphorus, provided that porcelain capsules are substituted for those made of metal. The porcelain has to be coated on the inside with fused potassium nitrate, which converts the phosphorus into P_2O_5 . This is then determined in the usual way. The author has applied this method to triethylphosphine, triphenylphosphine, aniline phosphite, &c., and has found it very rapid and quite safe.

MISCELLANEOUS.

Chemistry and Industry.—In the course of an interview in the *Jewish Chronicle*, Prof. Raphael Meldola, F.R.S., of the City and Guilds of London Institute, states that the Germans profited more from his aniline-dye discoveries than the English. "In scientific matters," he says, "the Germans are quicker to seize upon new ideas." Nevertheless, he is of opinion that English manufacturers are becoming alive to the assistance which the chemist can render them, and adds that there is a growing demand for chemists in various branches of industry. "Chemistry," he remarks, "is playing an ever more important rôle in industrial life, and has a finger in almost every industrial pie."

University College, Reading.—Mr. Percy C. Austin, late Scholar of Emmanuel College, Cambridge, is to be Lecturer in Chemistry. Mr. Austin graduated B.A. in 1901 (Natural Sciences Tripos) and M.A. in 1905. Since leaving Cambridge he has been engaged chiefly in chemical research in various countries. For two years he worked in conjunction with Professor Julius Schmidt in Stuttgart at nitroso-derivatives of amylene and at the nitration of phenanthraquinone, after which he was appointed, early in 1904, Research Assistant to Professor A. Senier at Queen's College, Galway (now University College, Galway), a post which he held for nearly four years. This period he devoted to a detailed investigation of acridines. In 1907 he was elected by the Royal Commissioners for the Exhibition of 1851 to a travelling research Scholarship. This he held first at University College, London, where he continued his work on complex acridines and on phenanthrene derivatives, and later at the Sorbonne in Paris, where he has been working until quite recently with Professor A. Haller on phenanthraquinone. The results of his investigations are published in numerous memoirs in the *Berichte der Deutschen Chemischen Gesellschaft* and in the *Journal of the Chemical Society*.

MEETINGS FOR THE WEEK.

FRIDAY, 12th.—Physical, 8. "Absorption Spectrum of Potassium Vapour," by P. V. Bevan. "Physiological Principles underlying the Flicker Photometer," by J. S. Dow. Exhibition of a Colour Perception Spectrometer, by F. W. Edridge-Green. "Tables of Ber and Bei and Ker and Kei Functions, with further Formulæ for their Computation," by H. G. Savidge.

THE CHEMICAL NEWS.

VOL C., No. 2607.

THE ESTIMATION OF CUPROUS OXIDE IN COPPER AND ITS ALLOYS.

By RICHARD HENRY GREAVES.

A NEW method for the determination of cuprous oxide in copper has recently been suggested by Coffetti (*Gazz. Chim. Ital.*, 1909, xxxix., 137). It depends on the fact that cuprous oxide is soluble in ammonia in the absence of oxygen, while copper is insoluble. Experiments made to

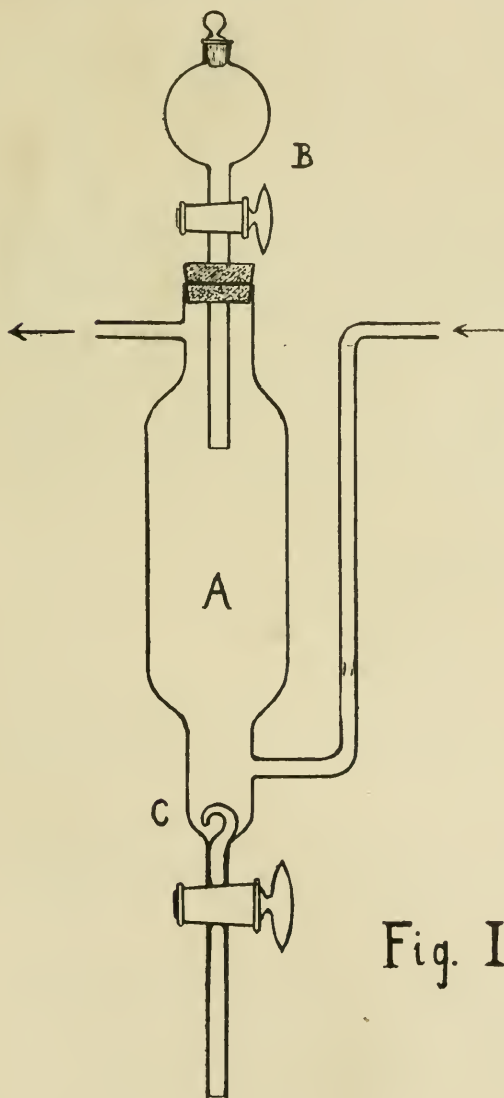


Fig. I

test the method have indicated certain limitations which it possesses, and have led to an improved form of apparatus for carrying out the estimation.

It must be remembered that the oxygen existing as

cuprous oxide in ordinary samples of copper is not the same as the total oxygen. For the determination of the latter, the copper in the form of fine drillings was heated in pure dry hydrogen, and the water formed was weighed (Archbutt, *Analyst*, 1900, xxv., 253).

The substances for analysis were synthetically prepared from pure electrolytic copper which contained 0.02 per cent of iron. The oxygen was introduced by the addition of cupric oxide; arsenic and antimony by rich alloys of each of these elements with copper. All the samples were analysed, and the total oxygen determined as above.

The apparatus used by Coffetti is shown in Fig. 1; his method was as follows:—The copper in the form of fine drillings or filings is introduced on to a pad of glass-wool to protect the syphon at c, and all air displaced by hydrogen which has been passed through ammonia solution to saturate it. Strong ammonia is then added through B, without interrupting the current of hydrogen. The apparatus is shaken from time to time, and the ammoniacal solution drawn off by the lower tube. The copper is washed with freshly boiled water containing 10 per cent of strong ammonia until the washings are colourless. The united solutions and washings are acidified with nitric acid, and the dissolved copper estimated electrolytically and calculated to cuprous oxide or oxygen.

It was found that the apparatus suffered from several defects, the chief of which was that the time taken for the solution of cuprous oxide was long (six to eight hours). Considerable pressure is required to keep up a steady stream of hydrogen through the liquid in A. To overcome these difficulties the form of tube shown in Fig. 2

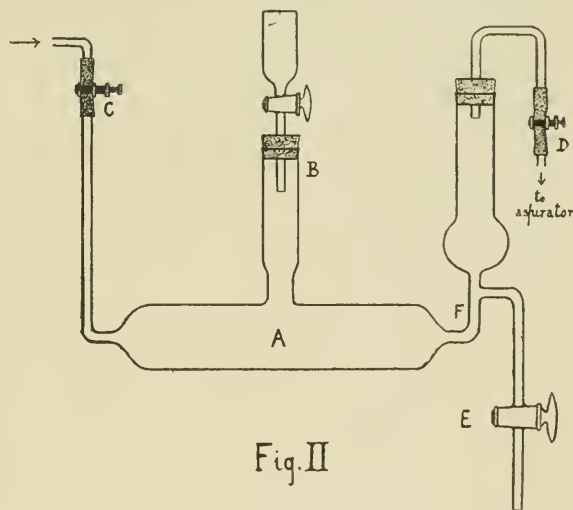


Fig. II

was adopted. The tube, A, was 3 cm. in diameter and 12 cm. long. Copper was introduced into the dry tube through B, and the air displaced by hydrogen. The hydrogen was obtained from a Kipp's apparatus, passed through silver nitrate solution and potash pumice, then through a heated plug of platinised asbestos, to convert any oxygen present into water, and was saturated with ammonia by passing it through a flask containing a small quantity of strong ammonia solution. The ammonia solution was warmed until the gas began to come off as a precaution against the possible presence of air; it was then added through B, and the operation carried out as described by Coffetti. The screw-clips at c and D served to regulate the hydrogen supply during the addition of the ammonia. To remove the solution the tap, D, is closed, the apparatus tilted, and E is opened, when the hydrogen forces the solution out. Cuprous oxide is said to dissolve in ammonia, giving a colourless solution, but the solutions obtained always had a distinct blue colour, which, on exposure to

TABLE A.
Per cent which dissolved.

No. of sample.	Amount taken. Grm.	Weight of Cu. Grm.	Weight of $Mg_2As_2O_7$. Grm.	Per cent which dissolved.		O calculated for As_2O_5 . Per cent.	O as oxide and arsenate. Per cent.	Total.	
				O.	As.			O.	As.
1.	0.50	0.0228	Trace	0.58	0.03 ?	0.016	0.60	0.62	0.03
2.	1.00	0.0218	0.0009	0.28	0.03 ?	0.016	0.30	0.31	0.03
3.	1.00	0.0048	0.0048	0.06	0.24	0.13	0.19	0.17	0.40
4.	1.00	0.0126	0.0074	0.16	0.36	0.19	0.35	0.36	0.51
5.	2.00	0.0080	0.0036	0.05	0.09	0.04	0.09	0.10	0.49

TABLE B.
Per cent which dissolved.

	Amount taken. Grm.	Weight of Cu. Grm.	Weight of Sb_2O_3 . Grm.	Per cent which dissolved.		O calculated for Sb_2O_3 . Per cent.	O as oxide and antimonate. Per cent.	Total.	
				O.	Sb.			O.	Sb.
1.	1.0	0.0069	0.0022	0.09	0.17	0.06	0.15	0.32	0.29
2.	1.0	0.0282	0.0010	0.36	0.08	0.03	0.39	0.41	0.10
3.	1.0	0.0152	0.0029	0.11	0.24	0.08	0.19	0.30	0.45

the air, developed the deep blue tint of the cupric compound. The initial blue colour may have been due to the action of the ammonia gas and water vapour on the copper before all the air was displaced, or to oxygen which found its way through the rubber connections; but the presence of a trace of oxygen does not appear to be harmful, and probably oxidised the cuprous compound to the cupric state before assisting in the dissolution of metallic copper. The final washings were allowed to stand in the air to see if a blue colour developed.

As stated, the apparatus must be dry to start with; if the copper is moist it is readily attacked by the ammonia gas before the air is removed, and a high result is obtained.

In this form of apparatus the copper is spread over a large surface; thus the duration of the experiment is warming the tube. The copper is allowed to settle after diminished, and can be still further reduced by gently shaking, so that there is no danger of getting it carried over out of the apparatus; if difficulty is experienced with small particles which remain in suspension, a very small plug of glass-wool at F will be found effective. The electrolysis was carried out, with a rotating cathode, in a solution containing 2 per cent nitric acid and 1 per cent sulphuric acid.

The method yielded the following results.—

(a) Pure Copper with Oxygen.

Amount taken. Grms.	Weight of copper. Grm.	Per cent O as Cu_2O .	Mean.	Total oxygen by combustion.
0.47	0.0652	1.761	1.762	1.775
0.50	0.0695	1.764		
1.00	0.0242	0.307	0.312	0.324
1.00	0.0249	0.316		
3.00	0.0065	0.040	0.039	0.036
3.00	0.0089	0.038		

(b) Copper with Arsenic.

The oxygen as Cu_2O is less than the total oxygen, and the solution was found to contain arsenic, which was estimated by the magnesia method. Since copper arsenide is insoluble in ammonia in the absence of oxygen, it appears that the arsenic existed as arsenate or arsenite. The former is in accordance with the results (see Table A).

Thus, assuming copper arsenate to be present, figures are obtained agreeing with the total oxygen, and to get the free Cu_2O a correction may be applied to the weight of copper deposited by subtracting the weight which exists as arsenate. Of course, this necessitates a determination of the arsenic in solution. The presence of the arsenic does not interfere with the deposition of the copper if proper conditions of current density, &c., are observed.

From the above data the proportions of arsenide, oxide, and arsenate can be calculated:—

Percentages of—

No. of sample.	Cu_2O .	Cu_3As .	$CuAsO_3$.
1.	5.12	—	0.07
2.	2.46	—	0.07
4.	1.08	0.53	0.89
3.	0.30	0.57	0.60
5.	0.32	1.01	0.21

These figures indicate that the oxide, arsenate, and arsenide come, or tend to come, into equilibrium in the copper, though the nature of the equilibrium is not clear, as the temperature of casting and conditions of cooling are uncertain.

(c) Copper with Antimony.

The remarks made with regard to arsenical copper apply equally to that containing antimony (see Table B).

In this case the oxygen calculated as oxide and antimonate falls short of the total oxygen; possibly free antimonous oxide exists in the copper.

The deposited copper contained a little antimony, and a correction was made for this.

(d) Copper with Iron.

Amount taken (grm.) 1.0

In the solution—

Weight of Cu (grm.) 0.0120

O as Cu_2O (per cent) 0.15

In the original sample—

Total O (per cent) 0.28

Fe (per cent) 0.41

A large amount of the oxygen exists as iron oxide. This may partially account for the discrepancy between the oxygen as Cu_2O , and the total oxygen in the series (a).

(e) Brass.

One grm. of an alloy containing about 70 per cent Cu to 30 per cent Zn, with 0.23 per cent oxygen, gave 0.0137 grm. of copper, equivalent to 0.18 per cent oxygen. The micro-structure showed fine filaments surrounding the crystals, presumably of zinc oxide.

(f) Bronze.

One grm. of bronze containing approximately 90 per cent Cu, 10 per cent Sn, with 0.32 per cent oxygen, gave 0.0108 grm. of copper, equivalent to 0.13 per cent oxygen as Cu_2O .

Heyn and Bauer have found by metallographic means that most of the oxygen in bronze exists as SnO_2 .

Summary.

The estimation of cuprous oxide by solution in ammonia has been examined, and a modified form of apparatus devised. For pure samples of copper it was found to give

excellent results; when the copper contains arsenic the results are too high, but an approximate correction may be calculated from the amount of arsenic dissolved, on the assumption that it dissolves as arsenate. The same applies to antimony. When iron is present in copper containing oxygen, a portion or the whole exists as oxide, and if the amount of iron present is large the cuprous oxide may become a comparatively unimportant constituent. On account of the purity of commercial copper at the present day, errors from the presence of antimony and iron will be small in practice. Brass and bronze also appear to yield good results; in the case of the latter the method is not so useful as would at first sight appear, as the oxygen exists mainly as SnO_2 , and it is this substance which exerts the deleterious influence on the properties of the alloy.

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THE ELECTROLYTIC PREPARATION OF THE AMALGAMS OF THE ALKALI AND ALKALI-EARTH METALS.*

By G. MCP. SMITH and H. C. BENNETT.

THE four methods by which alkali and alkali-earth amalgams have been prepared are:—1. Directly from metals. 2. By the action of an amalgam on a salt solution. 3. By the electrolysis of a complex alkali-mercury salt in aqueous solution, with platinum electrodes. 4. By the electrolysis of a salt solution with a mercury cathode.

The first method is satisfactory in the case of sodium and potassium amalgams, and is probably the best for the preparation of amalgams containing a high percentage of alkali metal (*cf.* Reuter, *Zeit. Elektrochem.*, 1902, viii., 801). It was employed by Kurnakov and Shukovski in the preparation of rubidium and caesium amalgams (*Zeit. Anorg. Chem.*, 1907, lii., 416); it was here necessary, however, to first prepare the free alkali elements. Lithium does not unite readily with mercury, and in the preparation of this amalgam from pure metallic lithium and mercury, at a high temperature, one of us met with a serious accident as the result of a violent explosion which took place upon the union of the two metals (G. McP. Smith, *Am. Chem. Journ.*, 1907, xxxvii., 506). A calcium amalgam of the formula CaHg_5 has also been prepared by this method (J. Schürger, *Zeit. Anorg. Chem.*, 1900, xxv., 425).

The second method was first employed by R. Böttger (*Journ. Prakt. Chem.*, 1834, i., 302) in the preparation of barium and strontium amalgams, which, however, he did not analyse, from sodium amalgam. It was also made use of by one of us for the same purpose (G. McP. Smith, *loc. cit.*). By means of it, Kraut and Popp likewise prepared potassium amalgam from sodium amalgam (*Ann. Chem.*, 1871, clix., 188); sodium amalgam may be even more readily prepared from potassium amalgam in the same way (G. McP. Smith, *loc. cit.*).

By means of the third method, the amalgams of ammonium and potassium have been prepared, with solutions of $(\text{NH}_4)_2\text{HgI}_4$ and K_2HgI_4 as electrolytes (Moissan, *Comptes Rendus*, 1907, cxliv., 730; G. McP. Smith, *Ber.*, 1907, xl., 2941).

The fourth method has frequently been employed in the preparation of these amalgams, and it is in many cases preferable to the other methods. The older electrolytic methods, however, require much time and somewhat complicated apparatus (Nernst, *Zeit. Elektrochem.*, 1897, iii., 308; Kerp, *Zeit. Anorg. Chem.*, 1898, xvii., 300; Kerp and Böttger, *Zeit. Anorg. Chem.*, 1900, xxv., 1; E. S. Shepherd, *Journ. Phys. Chem.*, 1903, vii., 29; G. McP.

Smith and J. R. Withrow, *Journ. Am. Chem. Soc.*, 1906, xxix., 320). This is especially true in the case of the method employed by Kerp (*loc. cit.*), and by Kerp and Böttger (*loc. cit.*) for the preparation of potassium, rubidium, and lithium amalgams).

The main difficulty encountered in the electrolytic preparation of these amalgams lies in the fact that the amalgams themselves are more or less readily decomposed by the solution which serves as the electrolyte. In certain cases, this action may take place to such an extent that the current efficiency soon approximates zero. In order to overcome this difficulty, Kerp and Böttger caused mercury to flow from the capillary end of a funnel, in the form of a thin thread, through a saturated solution of the alkali chloride. (Kerp and Böttger's method, which is undoubtedly the best of those cited, is recommended in Aebegg's "Handbuch der Anorg. Chem.," II. Band, 2 Abteilung, p. 579, for the preparation of these amalgams). The thread of mercury was made the cathode by means of a platinum wire which dipped into the funnel, and carbon rods, immersed in the solution, formed the anode. The vessel containing the electrolyte ended below in a syphon tube, so disposed that in flowing through it the amalgam offered a very small surface to the action of the solution. From the syphon tube, the amalgam flowed into a receiver provided with an outlet tube carrying a glass cock and connected with a dropping funnel. The liquid amalgam was transferred back to the capillary funnel by means of the dropping funnel, and was caused to repeat the circuit of the apparatus until it became too thick to flow in a continuous stream through the capillary, or until the evolution of hydrogen on the thread-like cathode became too rapid. The concentrated, semi-solid amalgam was then removed from the receiver, where it had gradually accumulated during the operation. During the electrolysis, dry hydrogen was kept above the amalgam in the capillary funnel, in the receiver, and in the dropping funnel, in order to prevent oxidation. As an example of the efficiency of this method, Kerp says that at 8 to 10 volts, 1000 grms. of mercury were converted in four or five hours into about 800 grms. of liquid, and 200 grms. of solid potassium amalgam, containing 0.45 per cent, and 1.5 per cent of potassium, respectively, and that during the electrolysis the liquid amalgam was made to repeat the circuit of the apparatus about 150 times. Kerp and Böttger state that rubidium amalgam can readily be prepared in the same way, but that the yield leaves something to be desired. With a saturated solution of lithium chloride and 1000 grms. of mercury, which went through the apparatus 100 times at 14 to 16 volts, they obtained, on filtering the product at 0°, 40 to 50 grms. of solid amalgam, containing 0.71 per cent of lithium; the mother-liquor contained 0.04 per cent of lithium.

Starting with the assumption that the rate of decomposition of the amalgam by the solution depends mainly upon the chemical nature of the amalgam itself, we have sought to obtain, in a simpler and less laborious manner, better yields of the pure amalgams. The efficiency of our method can be judged by comparing our yield of lithium amalgam, for example, with that of Kerp and Böttger. By it we electrolysed lithium chloride with 250 grms. of mercury as cathode for ninety minutes at 7 to 8.5 volts and 1.5 to 3.25 ampères, and obtained 105 grms. of solid, and 145 grms. of liquid amalgam, separated at the ordinary temperature.

The following is a description of the method which we have adopted.—In a 250 cc. beaker, with an internal diameter of 5.5 cm., a suitable quantity of mercury was made the cathode by contact with a platinum wire, fused through the end of a glass tube; the latter contained a little mercury, into which dipped the negative wire of the electric circuit. The mercury cathode was covered with a solution of a pure alkali or alkali-earth salt, into which dipped the platinum anode. This was a piece of heavy foil, 7.5 cm. in length and 2.1 cm. wide, bent at a right angle, so that the surface immersed (2.5 cm. x 2.1 cm.)

* Contribution from the Chemical Laboratory of the University of Illinois. From the *Journal of the American Chemical Society*, xxvi., No. 7.

was parallel with that of the mercury. The platinum anode was connected with a heavy copper wire by means of a brass connector, coated with paraffin to protect it from the action of the gas evolved. During the electrolysis, the current strength was read from a Weston standard ammeter; a standard voltmeter indicated the E.M.F. between the electrodes.

According to our experience, it is essential to employ very pure salts, since traces of certain impurities, such as iron and aluminium, greatly accelerate the interaction between the amalgam and the solution. The salts used in the following experiments were obtained from Kahlbaum. Shortly after starting the electrolysis, crystals of the specifically lighter solid amalgam begin to cover the surface of the cathode; these soon prevent the access of the metal deposited to the uncombined mercury underneath, so that hydrogen is rapidly evolved to the detriment of the current efficiency. This can at first be remedied by gently agitating the beater; as soon as the amalgam becomes pasty, however, it is necessary to push the crystals underneath by means of a flattened glass rod, bent at a right angle. In some cases the electrolysis can be continued until the amalgam becomes a solid mass of crystals, which can be lifted from the beaker without the separation of mother-liquor.

(NOTE.—The crystalline amalgams possess the property of absorbing considerable quantities of liquid amalgam without themselves becoming liquid. The liquid can be removed for the most part by filtration through chamois skin with suction; cf. Kerp, and Kerp and Böttger, *loc. cit.*.)

Cæsium Amalgam.—With 200 grms. of mercury as the cathode, a solution of 17 grms. of cæsium chloride in 50 cc. of water was electrolysed for eighty minutes at 6.5 volts and 2.6 ampères; the temperature rose during the process to 57°.

The resulting amalgam, after it had been washed with cold water and dried with filter-paper, was a liquid; but on setting down the dish containing the clean dry amalgam, crystals suddenly appeared on its surface, and, upon gently stirring, the whole mass became semi-solid, owing to the separation of crystals. After having stood for several days in a small glass stoppered bottle, the amalgam was filtered through chamois skin at 17°, in a Gooch crucible on the filter-pump; it gave 72 per cent of solid and 28 per cent of liquid amalgam. The solid amalgam in the lower part of the crucible held back a little mother-liquor with great tenacity.

(NOTE.—In all cases the clean dry amalgams were filtered as rapidly as possible, in order to avoid oxidation. The filtrates were caught in test-tubes, and placed in the suction flask, into which the Gooch funnel projected.)

Analysis.—I. Crystals near the top, 4.72 per cent Cs.; (II.) crystals near the bottom, 4.46 per cent Cs. The filtrate gave on analysis:—(I.) 2.74 per cent Cs.; (II.) 2.76 per cent Cs. The average composition of the mass was therefore 4.08 per cent, indicating a current efficiency of about 50 per cent.

(NOTE.—In the analysis of the solid amalgams, samples were taken from below the slightly oxidised surface at the top of the crucible. The amalgams were analysed by decomposition with 0.1 N. HCl in excess with methyl-orange as indicator, an excess of 0.1 N. NaOH was then added, and this was titrated back with 0.1 N. acid. Immediately preceding the end-point in the decomposition of an amalgam, a cloud of minute hydrogen bubbles was suddenly expelled from its surface, and the amalgam visibly shrank together. After this, on shaking the beaker, the mercury was broken up into small globules on striking the glass rod; the globules slowly coalesced on standing. This division did not take place as long as an appreciable quantity of alkali metal was present in the mercury; cf. G. McP. Smith, *Journ. Am. Chem. Soc.*, 1909, xxxi., 31.)

A second less concentrated preparation, which was liquid, did not crystallise perceptibly, even on the addition of a few crystals of the previously prepared solid amalgam. After twenty-four hours, however, it had separated into approximately one-third solid and two-thirds liquid amalgam.

(Kerp and Böttger observed an analogous phenomenon in the case of strontium amalgam; they did not work with cæsium amalgam).

Rubidium Amalgam.—With 100 grms. of mercury as the cathode, a solution of 10 grms. of RbCl in 50 cc. of water was electrolysed for forty minutes at 8 volts and 2.25 ampères. The temperature gradually rose to 54°.

On washing the pasty mass obtained at 54° with cold water, it became a solid cake, and could be picked up without the separation of any liquid. It was allowed to stand twenty-four hours in a small glass-stoppered bottle, after which it was filtered through chamois on the suction-pump at 19.5°, and gave 68 per cent of solid and 32 per cent of liquid amalgam.

The crystals gave on analysis 3.59 and 3.52 per cent Rb; the filtrate gave 1.22 and 1.20 per cent Rb.

From these figures the calculated rubidium content of the original amalgam was 2.81 per cent, indicating a current efficiency of about 60 per cent.

Potassium Amalgam.—With 250 grms. of mercury as the cathode, 50 cc. of saturated potassium chloride solution were electrolysed for fifty minutes at 6 volts and 3 ampères. On washing the warm semi-solid amalgam with cold water, it changed to a solid cake of fine needle-like crystals. This was dried between filter-paper, and at once analysed, giving 1.20 and 1.18 per cent K. The remainder of the amalgam was later filtered through chamois skin by suction; it gave 58.8 per cent of solid and 41.2 per cent of liquid amalgam. The separation was carried out at 20°.

Analysis.—Crystals, 1.70; filtrate, 0.46 per cent K.

(NOTE.—Kerp and Böttger obtained 1.55 per cent of potassium in the solid phase at 20°; in the liquid they, too, obtained 0.47 per cent at 20°.)

On calculation, these results give 1.20 per cent as the potassium content of the whole, showing that the first samples taken were representative. The current efficiency was therefore 83 per cent.

In order to see if a better yield could be obtained with potassium hydroxide as the electrolyte, a solution of 25 grms. of Kahlbaum's pure potassium hydroxide in 50 cc. of water was electrolysed for sixteen minutes at 4.5 volts and 3.8 to 4 ampères, until the evolution of hydrogen became stormy. The cathode was 125 grms. of mercury. The product, separated as before, gave 58.6 per cent of solid and 41.4 per cent of liquid amalgam. Although the concentration of the amalgam could be made no greater, the current efficiency approximated 100 per cent. A great deal of inconvenience was, however, experienced in stirring, owing to the mechanical transmission of alkali by the gases evolved.

Sodium Amalgam.—With 250 grms. of mercury as the cathode, 50 cc. of saturated sodium chloride solution were electrolysed for one hundred and five minutes at 6 volts and 3 ampères. The product formed a solid brittle mass of crystals. It was washed, dried with filter-paper, and analysed, giving 1.53 and 1.52 per cent Na. These figures indicate a current efficiency of 84 per cent.

The remainder of the amalgam was later filtered through chamois by suction at the ordinary temperature, and gave 72 per cent of solid and 28 per cent of liquid amalgam. The two phases were not analysed, but, according to Kerp and Böttger, they contain, at 25°, 1.76 per cent and 0.65 per cent of sodium, respectively. On calculation, these figures give 1.45 per cent as the sodium content of the whole, a value closely approximating that obtained by us.

Lithium Amalgam.—With 250 grms. of mercury as the cathode, 50 cc. of a saturated solution of lithium chloride were electrolysed for thirty minutes at 7 volts and 1.5 ampères, and then for sixty minutes at 8.5 volts and 3.25 ampères. It was found essential for the success of this preparation to keep the surface of the amalgam covered throughout the electrolysis with crystalline lithium chloride, and to keep the crystalline amalgam, which began to form in about twenty minutes, constantly pressed under the surface of the liquid amalgam. In all, 50 grms. of lithium chloride were added to the original saturated solution

during the electrolysis; this was necessary owing to the fact that the temperature rose to 70°.

The resulting amalgam was washed, dried, and analysed. It gave 0.398 and 0.397 per cent Li. These figures indicate a current efficiency of 88 per cent.

The remainder of the amalgam was filtered through chamois skin by suction; it gave 42 per cent of solid and 58 per cent of liquid amalgam. The separate phases were not analysed. Taking Kerp and Böttger's values, 0.70 per cent and 0.07 per cent for the composition of the solid and liquid phases, respectively, the calculated lithium content of the whole is 0.33 per cent, a figure which our result exceeds by about 20 per cent.

(NOTE.—The value 0.07 per cent was calculated by Kerp and Böttger for 25°; they made no experimental determinations between 0° and 64.5°).

We therefore repeated the experiment as follows:—

With 250 grms. of mercury as the cathode, the electrolysis was carried out as before for fifty-five minutes at 8.75 to 7 volts and 2.9 to 4 ampères (average about 3.5 ampères). The end temperature was 78°. The amalgam was then washed, dried, and allowed to stand for two days in a small glass-stoppered bottle, which it completely filled. On filtration it gave 27.9 per cent of solid amalgam. The separation was carried out at 22°.

The crystals, which were bright and unoxidised, gave on analysis 0.89 and 0.86 per cent Li.

The liquid amalgam gave, on analysis, 0.047 and 0.047 per cent Li.

These figures indicate a lithium content of 0.278 per cent in the amalgam as a whole; the current efficiency was therefore about 85 per cent.

If now we calculate the lithium content of the first preparation, taking our values of 0.875 per cent and 0.047 per cent as the lithium content of the solid and liquid amalgams, respectively, we arrive at the value 0.394 per cent, a figure in excellent agreement with our analytical results.

Barium Amalgam.—With 250 grms. of mercury as the cathode, 50 cc. of saturated barium chloride solution were electrolysed for two hours and twenty minutes at 7 to 6 volts and 1.75 to 2.1 ampères. The amalgam was very readily formed, and less attention was required than in the other cases. The amalgam, which could be lifted from the beaker without the separation of any liquid, was washed, dried with filter-paper, and analysed. It gave 3.49 and 3.48 per cent Ba. These figures indicate a current efficiency of about 78 per cent.

The remainder was filtered by suction, and gave 65 per cent of solid and 35 per cent of liquid amalgam. Taking 4.95 per cent and 0.34 per cent as the barium content of the solid and liquid, respectively (Kerp and Böttger's figures at 25°), the calculated barium content of the amalgam as a whole is 3.44 per cent. This is in good agreement with our analyses.

A second equally concentrated preparation was made in thirty-five minutes, by carrying out the electrolysis at 9 volts and 4½ ampères, with 185 grms. of mercury as the cathode.

Strontium Amalgam.—With 260.0 grms. of mercury as the cathode, a saturated solution of strontium chloride in 50 cc. of water was electrolysed for ninety minutes at 7.5 to 7 volts and 2.5 to 2.75 ampères. The end temperature was 43°. During the electrolysis the surface of the cathode was kept constantly covered with a layer of strontium chloride crystals. This is essential to the success of the preparation.

(NOTE.—Kerp and Böttger prepared strontium amalgam in a similar manner by the electrolysis of a saturated solution of strontium chloride. They state that the chlorate formed during the process greatly reduces the current efficiency, and to avoid this they renewed the solution several times during the electrolysis. This, however, is much less efficient in the production of a good yield of solid amalgam than the addition of crystalline strontium chloride).

The resulting amalgam, which was of a pasty consistency, was washed and then dried with filter-paper. It weighed

265.5 grms., the increase in weight indicating the presence of 2.07 per cent of strontium. The amalgam was kept for three days in a small glass-stoppered bottle; it was then washed, dried, and filtered, giving 52 per cent of solid and 48 per cent of liquid amalgam.

(NOTE.—Owing to a low water pressure at the time this amalgam was filtered, the separation of the mother-liquor was far from complete. Kerp and Böttger obtained a solid amalgam which contained 3.33 per cent of strontium).

The solid gave, on analysis, 2.80 and 2.82 per cent Sr; the filtrate gave 1.12 and 1.12 per cent Sr. The calculated strontium content of the amalgam as a whole is therefore 2.00 per cent. The current efficiency was 73 per cent.

Calcium Amalgam.—A saturated solution of calcium chloride was electrolysed with a mercury cathode, but the amalgam obtained was very dilute, and a great deal of a black mixture of calcium hydroxide with finely divided mercury was formed, especially around the platinum wire in the cathode. This broke the circuit after a short time. Several other solutions were tried, and the best results were obtained with a solution of re-crystallised calcium acetate, prepared from pure calcium carbonate and acetic acid.

With 250 grms. of mercury as the cathode, 35 cc. of saturated calcium acetate solution were electrolysed for forty minutes at 10 volts and 1.25 ampères. Hydrogen was rapidly evolved, although solid calcium acetate was added from time to time, and the solution darkened and foamed, so that constant stirring was necessary. After twenty minutes, white calcium hydroxide could be seen between the amalgam and the walls of the beaker, together with some dark spots, and the temperature had risen to 75°. The beaker was then immersed in cold water and the temperature kept at 35°; this, however, did not appear to diminish the action of the amalgam on the solution. After forty minutes, the E.M.F. was increased to 12.75 volts, which gave a current of 2.25 ampères. At the end of ten minutes more, the end of the glass tube and the platinum wire projecting from it, which dipped into the cathode, were completely covered with solid white calcium hydroxide; this broke the circuit, and the electrolysis was discontinued.

The amalgam was at once washed, dried, and analysed; it gave 0.091 and 0.092 per cent Ca. The current efficiency was therefore 29 per cent.

The remainder of the amalgam was filtered through chamois skin by suction, but no solid was obtained.

Upon comparing our yields of these amalgams with those of Kerp and Böttger, it will be seen that, by means of a simpler and much less laborious process, we have succeeded in obtaining far better results. The chlorine evolved during the electrolysis had no appreciable action on the platinum-foil, so it was not considered necessary to use a carbon anode.

In the analysis of the solid amalgams left behind on filtration, our results are in several instances higher than those obtained by Kerp and Böttger. This is especially true in the case of solid lithium amalgam, in which we obtained 0.875 per cent of lithium, while Kerp and Böttger found only 0.70 per cent. It is possible that, owing to the greater quantity of the solid amalgam at our disposal, the separation was more complete; we also increased the efficiency of the filtration, however, by alternately pressing the palm of the hand over the top of the Gooch crucible until the pressure became very low in the suction flask, and then lifting it off and allowing the air to rush through and sweep the mother-liquor along with it. This was repeated four or five times. The significance of our analytical difference can be seen from the fact that the formula LiHg_5 theoretically requires 0.70 per cent of lithium, while the formula LiHg_4 corresponds to 0.87 per cent. We have reason to believe that Kerp and Böttger did not succeed by filtration in entirely removing the mother-liquor from the crystalline amalgams, and we are repeating their work with the addition that we separate the last traces of the mother-liquor left behind on filtration, by means of a high-speed electric centrifugal machine. The results will be published in the near future.

A USEFUL OIL-BATH.

By LOUIS W. BOSART, Jun.

A MIXTURE of ten parts of refined cotton-seed oil and one part of beeswax makes a very satisfactory oil-bath. It emits very little fume below 250° C., and can be used safely almost throughout the range of the ordinary mercury thermometer, having a flash-point above 300° C. when heated in an open cup. A sample of hard paraffin under the same conditions flashed at 215° C.

The mixture has the advantage of the paraffin-bath that it solidifies on cooling, so that there is not the liability of the oil spilling out when not in use, and it has the added advantage that it melts quickly, and can be used almost immediately after heat is applied, as there is no hard cake that must first be melted as with paraffin.—*Journal of the American Chemical Society*, xxxi., No. 6.

GLASS-CUTTING BY MEANS OF AN ELECTRIC WIRE.

By FAREL L. JOUARD.

WHILE it is often necessary, in laboratory practice, to cut bottles and other glassware for the construction of special apparatus, the methods commonly used are somewhat tedious, besides requiring considerable manipulative skill for good results. The following simple device, however, will be found to combine rapidly with precision, even in the hands of an inexperienced operator. For some time the writer has been using it successfully, and, not knowing of its ever having been used before, publishes it with the idea that it might possibly be of interest to other experimenters.

The method consists in passing a current through a thin resistance-wire which has previously been wound about the glass vessel and carefully adjusted. For this purpose the 110-volt lighting circuit may be used, and, aside from the resistance-wire just mentioned, the only apparatus required is a couple of pieces of No. 18 insulated copper wire, a pair of ring-stands or other heavy objects, and a suitable rheostat. The vessel must be perfectly dry, and should have a scratch of about a quarter of an inch long made upon its surface, either on the emery-wheel or with a file, in order to provide a starting-point for the crack. After joining the ends of the resistance-wire to the copper leads, fixing the latter to the ring-stands at the desired height, and connecting the rheostat in series, the resistance-wire is fastened in a single loop around the glass vessel, so as to pass directly over the file-mark, and drawn taut by means of the ring-stands. A particle of asbestos paper is then inserted between the crossed ends of the loop, to prevent contact, and enough current is turned on to heat the wire to dull redness. In a few seconds a crack forms at the file-mark, and spreads rapidly around the vessel—frequently the crack starts and snaps across all at once; in either case, it will be found to have followed the path of the resistance-wire perfectly, so that the trueness of the fracture depends entirely on the smoothness and alignment of the wire.

Apart from the illustrations just given, which merely describes the cutting of a bottle in two, the method may equally well be applied to more intricate cases, where the fracture is to be a curve or a spiral.—*Journal of the American Chemical Society*, xxxi., No. 6.

Physical Society's Exhibition.—The date of the annual Exhibition held by the Physical Society of London, which was fixed some time ago for December 10, has been altered to Tuesday, December 14th, so that the Exhibition may be open in the afternoon as well as in the evening.

SOME FORMS OF FOOD ADULTERATION AND SIMPLE METHODS FOR THEIR DETECTION.*

By W. D. BIGELOW Chief of the Division of Foods,
and
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(Continued from p. 223).

SIMPLE TESTS FOR THE DETECTION OF FOOD ADULTERANTS.

Introduction.

GENERALLY speaking, the methods of chemical analysis employed in food laboratories can be manipulated only by one who has had at least the usual college course in chemistry; and some special training in the examination of foods is almost as necessary. Again, most of the apparatus and chemicals necessary are entirely beyond the reach of the home, and the time consumed by the ordinary examination of a food is in itself prohibitive.

Yet there are some simple tests which serve to point out certain forms of adulteration and can be employed by the careful housewife with the reagents in her medicine closet and the apparatus in her kitchen. The number may be greatly extended by the purchase of a very few articles that may be procured for a few cents at any drug store. In applying these tests, one general rule must always be kept carefully in mind. Every one, whether layman or chemist, must familiarise himself with a reaction before drawing any conclusions from it. For instance, before testing a sample of supposed coffee for starch, the method should be applied to a sample of pure coffee (which can always be procured unground) and to a mixture of pure coffee and starch prepared by the operator.

Many manufacturers and dealers in foods have the ordinary senses so highly developed that by their aid alone they can form an intelligent opinion of the nature of a product, or of the character, and sometimes even of the proportion, of adulterants present. This is especially true of such articles as coffee, wine, salad oils, flavouring extracts, butter, and milk. The housewife finds herself constantly submitting her purchases to this test. Her broad experience develops her senses of taste and smell to a high degree, and her discrimination is often sharper and more accurate than she herself realises. The manufacturer who has developed his natural senses most highly appreciates best the assistance or collaboration of the chemist, who can often come to his relief when his own powers do not avail. So the housewife, by a few simple chemical tests, can broaden her field of vision and detect many impurities that are not evident to the senses.

There are here given methods adapted to this purpose, which may be applied to milk, butter, coffee, spices, olive oil, vinegar, jams and jellies, and flavouring extracts. In addition to this some general methods for the detection of colouring matter and preservatives will be given. All of the tests here described may be performed with utensils found in any well appointed kitchen. It will be convenient, however, to secure a small glass funnel, about three inches in diameter, since filtration is directed in a number of the methods prescribed. Filter-paper can best be prepared for the funnel by cutting a circular piece about the proper size and folding it once through the middle and then again at right angles to the first fold. The paper may then be opened without unfolding in such a way that three thicknesses lie together on one side and only one thickness on the other. In this way the paper may be made to fit nicely into the funnel.

Some additional apparatus, such as test-tubes, racks for supporting them, and glass rods, will be found more convenient for one who desires to do considerable work on this subject, but can be dispensed with. The most convenient size for test-tubes is a diameter of from one-half to five-eighths inch and a length of from five to six inches. A graduated cylinder will also be found very convenient.

* Bulletin No. 100, Bureau of Chemistry, U.S. Department of Agriculture.

If this is graduated according to the metric system, a cylinder containing about 100 cc. will be found to be convenient; if the English liquid measure is used it may be graduated to from 3 to 8 ounces.

Chemical Reagents.

The word "reagent" is applied to "any substance used to effect chemical change in another substance for the purpose of identifying its component parts or determining its percentage composition." The following reagents are required in the methods here given:—

Turmeric paper.

Iron alum (crystal or powdered form).

Hydrochloric acid (muriatic acid) concentrated.

(*Caution.*—All tests in which hydrochloric acid is used should be conducted in glass or earthenware, for this acid attacks and will injure metallic vessels, such as iron, tin, zinc, &c. Care must also be taken not to bring it into contact with the flesh or clothes. If by accident a drop of it falls upon the clothes, ammonia, or in its absence a solution of saleratus or sal soda (washing soda), in water, should be applied promptly).

Iodine, tincture.

Potassium permanganate, 1 per cent solution.

Alcohol (grain alcohol).

Chloroform.

Boric acid or borax.

Ammonia water.

Halphen's reagent.

With the exception of the last reagent mentioned, these substances may be obtained in any pharmacy. The Halphen reagent should be prepared by a druggist rather than by an inexperienced person who desires to use it. This is especially important because of the inflammable nature of carbon bisulphide which enters into its composition.

(*Caution.*—Carbon bisulphide is a very inflammable substance and is at least as dangerous to handle as gasoline. For this reason the Halphen reagent, into the composition of which carbon bisulphide enters, must be handled with care, and only a small portion of it taken into the vicinity of the fire. When it is employed the end of the test-tube may be loosely stoppered with cotton. The carbon bisulphide in the amount of reagent used for a single test, however, is so small as not to cause any particular danger in its use).

Halphen's reagent is prepared as follows:—An approximately 1 per cent solution of sulphur is made by dissolving about one-third of a teaspoonful of precipitated sulphur in 3 or 4 ounces of carbon bisulphide. This solution mixed with an equal volume of amyl alcohol forms the reagent required by the method. A smaller quantity than that indicated by these directions may of course be prepared.

If turmeric paper be not available it may be made as follows:—Place a bit of turmeric powder (obtainable at any drug store) in alcohol, allow it to stand for a few minutes, stir, allow it to stand again until it settles, dip a strip of filter-paper into the solution, and dry it.

Determination of Preservatives.

The following methods cover all of the more important commercial preservatives with the exception of sulphites and fluorides. These are quite frequently used for preserving foods—the former with meat products and the latter with fruit products—but, unfortunately, the methods for their detection are not suitable for household use.

Detection of Salicylic Acid.—The determination of salicylic acid can best be made with liquids. Solid and semi-solid foods, such as jelly, should be dissolved, when soluble, in sufficient water to make them thinly liquid. Food-containing insoluble matter, such as jam, marmalade, and sausage, may be macerated with water and strained through a piece of white cotton cloth. The maceration may be

performed by rubbing in a teacup or other convenient vessel with a heavy spoon.

Salicylic acid is used for preserving fruit products of all kinds, including beverages. It is frequently sold by drug stores as fruit acid. Preserving powders consisting entirely of salicylic acid are often carried from house to house by agents. It may be detected as follows:—

Between 2 and 3 ounces of the liquid obtained from the fruit products, as described above, are placed in a narrow bottle holding 5 ounces, about a quarter of a teaspoonful of cream of tartar (or, better, a few drops of sulphuric acid) is added, the mixture shaken for two or three minutes, and filtered into a second small bottle. Three or four table-spoonfuls of chloroform are added to the clear liquid in the second bottle and the liquids mixed by a somewhat vigorous rotary motion, poured into an ordinary glass tumbler, and allowed to stand till the chloroform settles out in the bottom. Shaking is avoided, as it causes an emulsion which is difficult to break up. As much as possible of the chloroform layer (which now contains the salicylic acid) is removed (without any admixture of the aqueous liquid) by means of a medicine dropper and placed in a test-tube or small bottle with about an equal amount of water and a small fragment—a little larger than a pin-head of iron alum. The mixture is thoroughly shaken and allowed to stand till the chloroform again settles to the bottom. The presence of salicylic acid is then indicated by the purple colour of the upper layer of liquid.

Detection of Benzoic Acid.—Benzoic acid also is used for preserving fruit products. Extract the sample with chloroform as in the case of salicylic acid; remove the chloroform layer and place it in a white saucer, or, better, in a plain glass sauce dish. Set a basin of water—as warm as the hand can bear—on the outside window ledge and place the dish containing the chloroform extract in it, closing the window until the chloroform has completely evaporated. In this manner the operation may be conducted with safety even by one who is not accustomed to handling chloroform. In warm weather the vessel of warm water may, of course, be omitted. Benzoic acid, if present in considerable amount, will now appear in the dish in characteristic flat crystals. On warming the dish the unmistakable irritating odour of benzoic acid may be obtained. This method will detect benzoic acid in tomato catsup or other articles in which it is used in large quantities. It is not sufficiently delicate, however, for the smaller amount used with some articles, such as wine. It is often convenient to extract a larger quantity of the sample and divide the chloroform layer into two portions, testing one for salicylic acid and the other for benzoic acid.

Detection of Boric Acid and Borax.—Boric acid (also called boracic acid) and its compound with sodium (borax) are often used to preserve animal products, such as sausage, butter, and sometimes milk. For the detection of boric acid and borax, solids should be macerated with a small amount of water and strained through a white cotton cloth. The liquid obtained by treating solids in this manner is clarified somewhat by thoroughly chilling and filtering through filter-paper.

In testing butter place a heaping teaspoonful of the sample in a teacup, add a couple of teaspoonfuls of hot water, and stand the cup in a vessel containing a little hot water until the butter is thoroughly melted. Mix the contents of the cup well by stirring with a teaspoon, and set the cup with the spoon in it in a cold place until the butter is solid. The spoon with the butter (which adheres to it) is now removed from the cup and the turbid liquid remaining strained through a white cotton cloth, or better, through filter-paper. The liquid will not all pass through the cloth or filter-paper, but a sufficient amount for the test may be secured readily.

In testing milk for boric acid two or three table-spoonfuls of milk are placed in a bottle with twice that amount of a solution of a teaspoonful of alum in a pint of water, shaken vigorously, and filtered through filter-paper. Here again a clear or only slightly turbid liquid passes through the paper,

About a teaspoonful of the liquid obtained by any one of the methods mentioned above is placed in any dish, not metal, and five drops of hydrochloric (muriatic) acid added. A strip of turmeric paper is now dipped into the liquid and then held in a warm place—near a stove or lamp—till dry. If boric acid or borax was present in the sample the turmeric paper becomes bright cherry-red when dry. A drop of household ammonia changes the red colour to dark green or greenish black. If too much hydrochloric acid is used the turmeric paper may take on a brownish red colour even in the absence of boric acid. In this case, however, ammonia changes the colour to brown just as it does turmeric paper which has not been dipped into the acid solution.

Detection of Formaldehyde.—Formaldehyde is rarely used with other foods than milk. The method for its detection in milk is given elsewhere. For its detection in other foods it is usually necessary to first separate it by distillation, a process which is scarcely available for the average person without laboratory training and special apparatus. For this reason no method is suggested here for the detection of formaldehyde in other foods than milk.

Detection of Saccharin.—Saccharin has a certain preservative power, but it is used not so much for this effect as because of the very sweet taste which it imparts. It is extracted by means of chloroform, as described under the detection of salicylic acid. In the case of solid and semi-solid foods, the sample must, of course, be prepared by extraction with water, as described under salicylic acid. The residue left after the evaporation of the chloroform, if a considerable amount of saccharin is present, has a distinctly sweet taste.

The only other substance having a sweet taste which may be present in foods, *i.e.*, sugar, is not soluble in chloroform, and therefore does not interfere with this reaction. Certain other bodies (tannins) which have an astringent taste are present, and as they are soluble in chloroform may sometimes mask the test for saccharin, but with practice this difficulty is obviated.

(To be continued.)

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

THE following completes the abstracts of Papers received during the vacation and published or passed for publication in the *Transactions* :—

206. "*The Formation at High Temperatures of some Refractory Metals from their Chlorides.*" By JOHN NORMAN PRING and WILLIAM FIELDING. (*Trans.*, 1909, 1497).

The authors have investigated the reactions whereby some refractory metals can be prepared by exposing the vapour of their volatile chlorides to electrically heated carbon rods or filaments.

With tungsten chloride, used alone, under diminished pressure, decomposition took place in contact with the carbon rod at temperatures between 1200° and 1500°, and with molybdenum, below 1300°, forming adherent deposits on the rods of the pure metals. Above these temperatures the carbides resulted. In presence of small quantities of water vapour, the metals were always obtained free from the carbides.

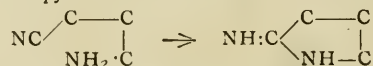
Boron and silicon were obtained from their chlorides by exposing these together with hydrogen to the heated carbon rods. Pure crystalline silicon was obtained at temperatures between 1700° and 1850°. A thin protective layer of the carbide which first formed on the rod prevented carbonisation of the subsequent deposit, until, at a temperature of about 1900°, the carbide alone resulted.

With boron, the deposit always consisted of the carbide

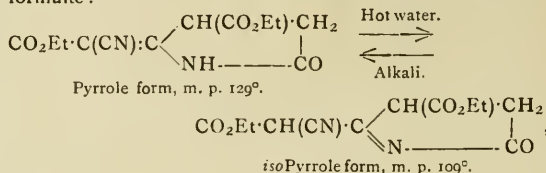
(B₆C), which was formed at temperatures between 1800° and 2000°. Some approximate photometric measurements were made on the radiating properties of the metal-coated rods. A very large increase in the luminosity for a given power-expenditure was observed with tungsten and molybdenum, amounting to about three times that of the carbon, whilst very little difference was produced by the deposits of silicon and boron carbide.

207. "*The Formation and Reactions of Imino-compounds. Part. X. The Formation of Imino-derivatives of Pyrrole and of isoPyrrole from Amino-nitriles.*" By STANLEY ROBERT BEST and JOCELYN FIELD THORPE. (*Trans.*, 1909, 1506).

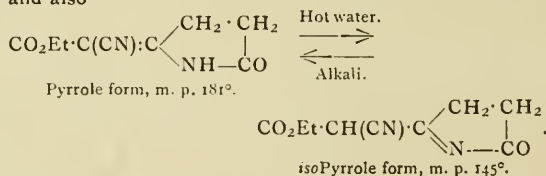
The authors have discovered that open-chain compounds having an amino-group in the γ -position with respect to a nitrile group, pass on treatment with sodium ethoxide into derivatives of pyrrole in accordance with the scheme :—



It is also found that those ketones, derived from these imino-compounds, which have a carbon atom adjacent to the nitrogen, doubly linked outside the ring, tend readily to pass into the isomeric compound having the bond in the ring, the two compounds being mutually convertible the one into the other. This is shown by the following formulæ :—



and also



208. "*The Atomic Weight of Chlorine.*" By ROBERT WHYTLOW GRAY and FRANK PLAYFAIR BURT. (*Trans.*, 1909, xxiv., 1633).

The value for the weight of a normal litre of hydrogen chloride resulting from twenty-one experiments is 1.63915 grms., Lat. 45°. The value previously published (*Proc.*, 1908, xxiv., 215) was slightly too low.

Two volumes of hydrogen chloride, when decomposed by red-hot aluminium in a specially constructed apparatus, were found to yield 1.0079 volumes of hydrogen, the gases being measured at 0° and 760 mm. Eight experiments were made, and the maximum deviation was 1 part in 5000.

The atomic weight of chlorine calculated from these numbers, assuming that the atomic weight of hydrogen is 1.00762 (Morley) and that the density of hydrogen is 0.089873 grm. per litre at 0° and 760 mm., Lat. 45°, is 35.459; O = 16.

The authors have also measured the form of the *p**v* isothermal of hydrogen chloride at 0° between the pressure limits of 800 and 160 mm. The amounts of gas absorbed by the glass surfaces of the apparatus at different pressures were experimentally determined, and the observed *p**v* values were corrected. Similar measurements with oxygen were also made in the same apparatus. Graphic extrapolation gave for the mean coefficient of compressibility between 1 and 0 atmosphere pressure at 0° :—

For oxygen $A'_0 = 0.000964$,
,, hydrogen chloride $A'_0 = 0.00748$,

for the molecular weight of hydrogen chloride on the oxygen standard, 36.469, and for the atomic weight of chlorine,

35·461. The value of the atomic weight resulting from the volumetric analysis, namely, 35·459, is thus confirmed.

It is hence concluded that 35·460 is a close approximation to the true atomic weight of chlorine.

209. "isoQuinoline Derivatives. Part II. The Constitution of the Reduction Products of Papaverine." By FRANK LEE PYMAN. (*Trans.*, 1909, 1610).

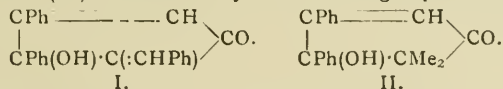
Goldschmidt (*Monatsh.*, 1886, vii., 485; 1898, xix., 324) obtained by the reduction of papaverine a crystalline base melting at 200—201° which he termed "tetrahydropapaverine," together with an amorphous base from which no crystalline derivative was obtained.

The author has shown that this amorphous base is identical with the "isotetrahydropapaverine" obtained by Freund and Beck (*Ber.*, 1904, xxxvii., 3321) by the reduction of papaveraline, and is in reality *tetrahydropapaverine*. It forms crystalline salts of the formula $C_{20}H_{25}O_4N.HX$, and yields an *N*-benzoyl derivative, which gives on oxidation a new base, 6:7-dimethoxy-3:4-dihydroisiquinoline. The methochloride of this is identical with 6:7-dimethoxy-2-methyl-3:4-dihydroisiquinolinium chloride, a salt obtained by the action of hydrochloric acid on 4:5-dimethoxy-2-β-methylaminoethylbenzaldehyde (prepared by the oxidation of laudanose; compare Pyman, *Trans.*, 1909, xcv., 1266). Further, proof that the amorphous base is tetrahydropapaverine is afforded by the fact that it yields laudanose on methylation.

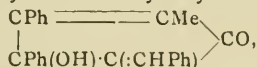
Analyses of Goldschmidt's so-called "tetrahydropapaverine" and its derivatives show that this base has the formula $C_{20}H_{23}O_4N$, and is in reality 1:2-dihydro-papaverine.

210. "Direct Proofs of the Presence of the Hydroxyl Group in Derivatives of Anhydroacetonebenzil." By FRANCIS WILLIAM GRAY.

The author has succeeded in acetylating benzylidene-anhydroacetonebenzil (I.) and ββ-dimethylanhydroacetonebenzil (II.) with acetic anhydride containing sulphuric acid.



For the formation of an acetyl derivative of the anhydroacetonebenzil series, it is essential that both hydrogen atoms of the methylene group should be displaced, but in the case of benzylidene-α-methylanhydroacetonebenzil—

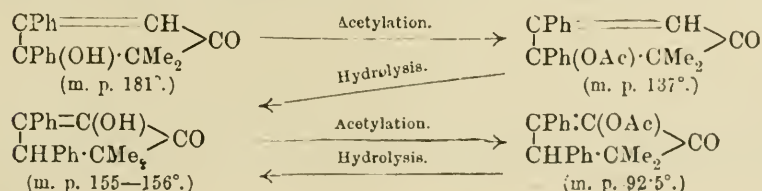


no acetyl compound but a dehydration derivative is obtained.

Direct proof of the presence of the hydroxyl group in α-methylanhydroacetonebenzil and in benzylidene-α-methylanhydroacetonebenzil was afforded by the preparation of their ethyl ethers. The conclusion is drawn, that ethyl ethers can be obtained by the method used (boiling with ethyl alcohol and sulphuric acid) only with compounds in which the hydrogen atom of the CH group of anhydroacetonebenzil is displaced by a methyl group.

211. "Isomerides of Anhydroacetonebenzil and its Derivatives." By FRANCIS WILLIAM GRAY.

The acetyl derivatives of ββ-dimethylanhydroacetonebenzil and benzylideneanhydroacetonebenzil (see preceding paper) on hydrolysis give isomerides of these compounds. The reactions may be represented as follows:—



212. "The Constitution of Glucose Derivatives." Part II. Condensation Derivatives of Glucose with Aromatic Amino-Compounds." By JAMES COLQUHOUN IRVINE and ROBERT GILMOUR. (*Trans.*, 1909, 1545).

In continuing their previous work (*Trans.*, 1908, xciii., 1429) on the constitution of sugar derivatives, the authors have condensed glucose with a number of aromatic amino-compounds, obtaining mutarotatory stereoisomeric forms of glucose-β-toluidide, glucose-β-naphthylamide, glucose-β-phenetide, and glucose-α-carboxyanilide.

The compounds mentioned undergo mutarotation comparable in every way with that shown by glucoseanilide, for which the γ-oxidic structure has been established by a synthetical method. The results indicate that all the compounds must be similarly constituted, and that, so far as the cases examined are concerned, the normal condensation of glucose with amino-acids or bases consists in the elimination of water from the amino group and the hydroxyl group attached to the terminal carbon atom of the sugar molecule.

The following compounds were isolated in pure stereochemical forms:—

α-Glucose-p-toluidide: anhydrous prisms, $[\alpha]_D^{20} + 181·9^\circ \Rightarrow -45·0^\circ$.

β-Glucose-p-toluidide: needles containing 1H₂O, $[\alpha]_D^{20} 97·6^\circ \Rightarrow -45·2^\circ$; plates containing $\frac{1}{2}$ H₂O, $[\alpha]_D^{20} 94·6^\circ \Rightarrow 47·3^\circ$.

β-Glucose-p-phenetide: needles containing 1H₂O, $[\alpha]_D^{20} 96·1^\circ \Rightarrow -38·3^\circ$.

β-Glucose-β-naphthylamide: needles containing 1H₂O, $[\alpha]_D^{20} -118·7^\circ \Rightarrow 48·1^\circ$.

α-Glucose-α-carboxyanilide: needles containing 1H₂O, $[\alpha]_D^{20} + 87·4^\circ \Rightarrow +14·5^\circ$.

213. "The Relation between Viscosity and Chemical Constitution. Part IV. Viscosity and Hydration in Solution." By ALBERT ERNEST DUNSTAN and FERDINAND BERNARD THOLE. (*Trans.*, 1909, 1556).

The authors have determined the viscosity-concentration curves for the binary systems composed of water and methyl, ethyl, and propyl alcohols, and acetic acid respectively at different temperatures. They confirm the results of previous investigators, and discuss the nature of the mixtures of maximum viscosity, particularly with respect to the temperature-coefficient of viscosity.

214. "Some Derivatives of l-Benzoin." By HENRY WREN. (*Trans.*, 1909, 1583).

d-Mandelamide and d-benzoin have been isolated and found to agree in their properties with l-mandelamide and l-benzoin. A number of optically active derivatives of l-benzoin have also been prepared.

215. "Racemisation Phenomena observed in the Study of l-Benzoin and its Derivatives." By HENRY WREN. (*Trans.*, 1909, 1593).

It has been shown that l-benzoin and its methyl ether readily racemise under the action of potassium hydroxide or sodium ethoxide, this being probably due to a desmotic change within the molecule. l-Benzoin ethyl ether was found to be partly, and carbanilido-l-benzoin completely, racemised by heat, whilst under the action of benzoyl chloride at a rather high temperature, of aniline at 100°, and of a saturated solution of hydrogen chloride in alcohol at a temperature not exceeding 40°, l-benzoin has been converted into derivatives of r-benzoin.

Finally, methyl l-mandelate has been found to undergo partial racemisation during its conversion into l-mandelamide by the action of alcoholic ammonia. The acetylation of l-benzoin-α-oxime has also been effected.

216. "Diketodiphenylpyrroline and its Analogues." By SIEGFRIED RUHEMANN. (*Trans.*, 1909, 1603).

The author has continued his work on the interaction of the

sodium derivatives of aromatic amides with ethyl phenylpropionate (*Trans.*, 1909, xcv., 984), and has prepared a number of analogues of diketodiphenylpyrroline, $\text{CO}-\text{CO}$ $\begin{array}{c} | \\ \text{CPh:CPh} \end{array} \text{NH}$. These substances have a deep colour, which varies from dark red to brown and black, and have the property in common that they dissolve in dilute alkalis to yield blue solutions, which, however, rapidly turn yellow. They resemble, therefore, isatin, and, like this form, phenylhydrazones and oximes.

In this connection the author has examined the behaviour of phenylcarbamide and *p*-tolylcarbamide towards ethyl phenylpropionate, and has found that this reaction, unlike that in which carbamide is used, does not give rise to cyclic compounds, but colourless acyl derivatives of carbamide, for example, phenylpropionylphenylcarbamide, $\text{C}_6\text{H}_5\cdot\text{C}:\text{C}:\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$.

217. "The Synthesis of Acridines: Tetramethylacridines, Dimethylnaphthacridines, Naphthaquinacridines, Diquinacridines." By ALFRED SENIER and ARTHUR COMPTON. (*Trans.*, 1909, 1623).

By further employment of the methods described in a previous paper (*Trans.*, 1907, xci., 1927), the authors have obtained 2:3:7:8-tetramethylacridine, and also the corresponding 9:10-dimethylpheno-

$\begin{array}{c} \text{N}\cdot\beta \\ \text{CH}\cdot\alpha \end{array}$

-naphthacridine and

$\begin{array}{c} \text{N}\cdot\alpha \\ \text{CH}\cdot\beta \end{array}$

9:10-dimethylpheno-|-naphthacridine. The chief ob-

ject of this inquiry, however, was to prepare acridines with heterocyclic wings, and three heterocyclic acridines, namely,

$\begin{array}{c} \alpha\cdot\text{N}\cdot\beta \\ \beta\cdot\text{C}\cdot\gamma \end{array}$

6-N-6|-diquinacridine, 6-N-6|-naphthaquinacridine, and 5-CH-5|-naphthaquinacridine, have been isolated by the

use of aminoquinolines.

The diquinacridine described is the first known member of a group of twenty-one possible isomeric diquinacridines derived from ordinary quinoline, and, similarly, the two naphthaquinacridines belong to a group of heterocyclic acridines of which eighteen members are theoretically possible.

All these compounds, containing as they do the acridine fluorophoric group, exhibit marked fluorescence. When dissolved in the usual organic solvents, the ultraviolet waves are so reduced in refrangibility that they appear in the blue, whereas in solution in glacial acetic or concentrated sulphuric acids they are reduced as far as the green, or even yellowish green, portion of the spectrum.

PHYSICAL SOCIETY.

Ordinary Meeting, October 22nd, 1909.

Dr. C. CHREE, F.R.S., President, in the Chair.

MR. F. E. SMITH read a paper entitled "On Cadmium Amalgams and the Weston Normal Cell."

Cadmium amalgams may be solid, liquid, or a mixture of solid and liquid phases, the percentage composition of the phases depending on the temperature. When a completely liquid amalgam is cooled below the lower transition temperature, the centre of the resulting solid is of high cadmium concentration, and the outer skin of low cadmium concentration. Diffusion tends to produce uniformity, and in consequence the E.M.F. of a cell containing the amalgam is unstable for a considerable length of time. When the amalgam is slowly cooled to a temperature a little below the lower transition temperature, the difference of concentration between the inner and outer

parts of the amalgam need be only small to enable the outer skin to be a two-phase system. The diffusion process will be slow, and the E.M.F. may remain constant for a very long time. Amalgams which were of uniform cadmium concentration throughout were obtained by chilling completely liquid amalgams to a temperature of about -50°C .; although not initially stable, rapid diffusion processes resulted in these amalgams becoming approximately uniform throughout after a few days, and their electromotive properties were markedly different from those of slowly cooled amalgams. If, however, the temperature of such an amalgam is raised until two phases exist, subsequent cooling will not restore the uniform condition, and an unstable amalgam results. The experiments indicate that a 12.5 per cent amalgam may be safely used at all temperatures between 12° and 60°C ., and a 10 per cent amalgam at all temperatures between 0° and 51°C . Experiments were made on the temperature coefficients of the anode and cathode limbs of the Weston normal cell, and show that if a difference of temperature of 1°C . exists an error of about 3 parts in 10,000 is introduced.

Mr. S. W. J. SMITH expressed his admiration of the paper as a further example of the author's great experimental skill. The author had confined himself almost entirely to a careful and detailed account of his experiments, but it seemed that the results would have been easier to assimilate and more interesting (although not more important) if some further attempt had been made to supply a theoretical basis. So far as he (the speaker) could judge, many of the results could be explained very simply by means of well known generalisations fixing the conditions of equilibrium in systems such as those with which the author had worked. The results corroborated (and exhibited the value of) the scheme of equilibrium for cadmium amalgams first proposed by Roozeboom in connection with the experiments performed under his direction by Bijl. Their discussion from this point of view would occupy more time than was at his disposal, and could be postponed. It might serve a useful purpose, however, if he were to ask for a more explicit opinion on one point. In a series of amalgams (of different percentage compositions) yielding the same E.M.F. at a given temperature, he (the speaker) did not think it was necessary, in order to avoid electrolytic effects, that the whole surface of each amalgam should be fluid. In the stable two-phase amalgams, it appeared to him that (so far as electrolytic action was concerned) the solid and liquid phases could co-exist in contact with the solution. In unstable amalgams, cooled rapidly to the temperature of experiment, containing a greater percentage of cadmium than either component of the two-phase system, and yet partially fluid, he thought the tendency of electrolytic action (as of diffusion) would be to reduce the amount of fluid amalgam in the surface-layer.

In reply, Mr. F. E. SMITH said he was glad to know that the results were in agreement with phenomena common to alloys of the binary system. The difficulty of obtaining perfectly stable amalgams necessitated caution in the interpretation of the results, and in many instances when, according to the theory of alloys, there should have been perfect agreement in the electromotive properties of a series of amalgams, small but decided differences had been observed. With increasing time these differences might disappear.

With regard to the state of the anode surface, he did not wish to imply that in stable two-phase amalgams the whole of the surface was in a fluid condition, but with unstable amalgams which were part solid and part liquid, he thought the evidence was in favour of such a surface.

A paper entitled "Production of Radium from Uranium" was read by Mr. SODDY.

The measurements on the growth of radium in the three uranium solutions purified by Mr. T. D. Mackenzie between three and four years ago have shown that in all the growth of radium is proceeding at a rate proportional to the square of the time within the error of measurement. The methods of testing have been improved and the

ordinary error is not greater than 10^{-12} grm. of radium. This result indicates the existence of only one long-lived intermediate product in the series between uranium and radium. The period of average life of this body, calculated on the assumption that no other intermediate bodies exist, is 18,500 years in the case of the oldest solution for which data are available over a period from the end of the third to the end of the fourth year from purification. But for the solution prepared last, over a period from the end of the second to the end of the third year, the period indicated is about half again as long as in the first experiment. Indeed, had this solution grown radium at the same rate, with reference to the square of the time, as the older solution has been during the past year, more radium should have been formed than the total amount now actually present. This suggests the existence of at least one new intermediate product in the series "Uranium A" with a period comparable to the time observations have been in progress. From a mathematical investigation of the effect of such a body on the rate of growth of radium, it is concluded that it would not, if it existed, appreciably alter the production of radium according to the square of the time over the period accurate observations have been made, even were the period of the new body as great as four years. But its existence would vitiate the calculation of the period of the direct parent of radium according to the simple formula neglecting short-lived products. Other evidence on the problem is contained in the next paper ("Rays and Product of Uranium X").

A paper entitled "*The Rays and Products of Uranium X*" was ready by Mr. SODDY.

Experiments have been made with the Uranium X preparations separated with the help of Mr. A. S. Russell from 50 kilograms of pure uranyl nitrate (*Phil. Mag.*, Oct. 1909, p. 620). There occurred the growth of a feeble α -radiation as the intense β -radiation decayed. Such a growth of α -rays, concomitant with the decay of β -rays, is to be expected if the parent of radium is the direct product of uranium X. From the period of the parent of radium given in the last paper, the uranium X in equilibrium with 1 kilogram of uranium should give by its complete disintegration a product having the α -activity of 2 mgrms. of uranium, if no new intermediate bodies intervened.

The preparations of uranium X were examined in a magnetic field sufficient to deviate all rays having a value for H_0 less than 8640, but the still undeviated β -radiation produced a leak in the electroscopes several times greater than that due to the γ -rays. So far as can be seen, these difficultly deviable β -rays are similar in general character and in the value of their absorption coefficient to ordinary β -rays. The first measurements were made in an electroscop filled with air, by covering the preparation with a thin screen, sufficient to absorb α -rays, and measuring the difference between the leaks with and without the screen. The results of these experiments are believed now to be untrustworthy, and they are rejected provisionally. In later experiments the electroscop was filled with hydrogen, which constituted an enormous advance, and these experiments have shown that the α -radiation of the preparation remains sensibly constant as the β -radiation decays. Anomalies have been encountered with the difficultly deviable β -radiation, which appears to vary in intensity according to the conditions in an unexplained way. But throughout, the "difference leak" between the preparation bare and covered, due to α rays, has remained constant in all the preparations examined. These measurements of the α -rays, for different preparations, cover a period from immediately after preparation to nearly a year in the case of the main preparation, and longer periods in the case of weaker preparations. The two most recent preparations each contained the uranium X in equilibrium with about 5 kilograms of uranium, and the growth of α -rays if the change of uranium X into the parent of radium were direct, should be equal to the α -radiation of 10 mgrms. of uranium. This should have been easily detectable under the con-

ditions of the experiment. It is concluded that the parent of radium cannot be the direct product of uranium X. The experiments, taken in conjunction with those given in the preceding paper, indicate that it is not a product of uranium X at all, but the subsequent history of the uranium X preparations must be awaited before this can be decided.

A paper entitled "*The Production of Helium from Uranium and Thorium*" was read by Mr. SODDY.

Helium has been detected in four experiments with uranium, in three with thorium, and in one with pitchblende solutions carried out according to the methods already published (*Phil. Mag.*, Oct., 1908, p. 513). Recent experiments with nearly a year's accumulation of helium from about 2 kilograms of uranium and thorium respectively have ended in failure owing to accidents. For this reason the quantitative estimate of the rate of production of helium is no further advanced than has already been published (*Phys. Zeit.*, 1909, x., 41).

Prof. STRUTT remarked that the author's experiments covered much ground, and suggested many interesting questions. He congratulated Mr. Soddy upon the skill with which he had attacked the subject, and referred to the difficulty of carrying out successfully complicated experiments which extended over long periods of time. With reference to the experiments on the growth of radium, he asked the author what was the ratio between the amount grown and the actual quantity present at the start, and also what multiple was the final leak of the electroscop of the normal air-leak. With regard to detecting the growth of α -radiation in the presence of β -radiation, he suggested that the scintillations produced by α -rays on a phosphorescent screen might be made use of. Referring to the experiment on the growth of helium in sylvine, Prof. Strutt remarked that he would have been astonished if the author had obtained any evidence of the production of helium in the comparatively short time over which his experiments extended.

The CHAIRMAN drew attention to one of the formulæ used by the author in which the "time" occurred as the "square." He asked if this formula held good when the time considered was large.

Mr. SODDY, in reply, said the natural leak of the electroscop was 1.1 (divisions per minute), and the leak due to the radium in the oldest preparation at the end of the fourth year was 4.2. The initial value found by extrapolation from the curve shown, in which quantity of radium was plotted against the square of the time, was 2.1. The initial value found experimentally as the mean of the first nine observations extending over the first nine months, when the methods were less sensitive than now, was 2.7. This bears out the view that a new intermediate body exists, retarding the initial rate of production of radium, though no great weight can be attached to the initial observations.

Prof. Strutt's suggestion that the α -radiation of uranium X preparations should be examined by the scintillation method might prove a valuable one, though on account of the impossibility of entirely removing β -rays it had not so far been attempted.

With reference to sylvine, the crystalline character of the mineral rendered it open to question whether helium if generated would be retained. In addition the radioactivity of potassium had suggested the experiment. No doubt a production of helium sufficient to detect would be remarkable, but it seemed worth looking for.

Answering the Chairman's question, the theoretical law, that the production of radium should proceed at a rate proportional to the square of the time, only referred to the initial rate of production, that is for periods of observation short in comparison with the period of average life of the direct parent of radium. The latter must be many thousands of years, and the law referred to should hold accurately over a far longer period than could be examined in the lifetime of a single observer.

RÖNTGEN SOCIETY.

THE annual Presidential Address before the Röntgen Society was delivered on November 4th, when Mr. C. E. S. PHILLIPS, F.R.S., Edin., gave a general survey of the recent developments in radiography, and concluded by describing an arrangement of his own for more efficiently measuring X-ray radiation. A good many people were still nervous, he said, about X-ray burns, although the experts were agreed that in these days burning, when it occurred, was due either to the carelessness of the operator or to his ignorance. He thought it would be as well if the Council of the Röntgen Society would issue an authoritative and reassuring statement on this matter. In dealing with progress on the physical, as distinct from the medical, side of X-ray work, he devoted special attention to the work of Barkla and Sadler, of the George Holt Physics Laboratory at Liverpool. The great stumbling-block in the path of X-ray investigation had hitherto been the heterogeneity of the beams, and Barkla and Sadler found that each of nine given elements, when subject to a suitable primary beam of X-rays, emitted an almost perfectly homogeneous beam of rays, the penetrating power of which was characteristic of the element emitting it. The nine homogeneous beams of rays thus produced would be of the greatest value in the study of X-ray phenomena. This, said Mr. Phillips, was exactly what was wanted. Sadler was now at work upon the problem of secondary radiation.

In speaking of radio-activity, Mr. Phillips said that any further study of cell development must take into account the effects of atomic disintegration. There was strong evidence that all matter was radio-active, and on this subject Dr. Lazarus-Barlow, the Director of the Cancer Research Laboratory of the Middlesex Hospital, had arrived at some startling conclusions, which it was hoped he would bring before the Society at the January meeting. The President thought that in the great amount of interest that the question of radio-activity was exciting, the share which England had in the discovery of the phenomenon was too often passed over and forgotten. At about the same time that Becquerel made his discovery, Professor Silvanus Thompson, working on different lines from those of his French contemporary, also discovered the phenomenon. In June, 1896, Thompson placed small quantities of fluorescent substances upon a thin aluminium shutter behind which stood a photographic plate. The arrangement was left in the sun for several hours, and on development the plate showed dark patches, England, then, shared with France in the credit attaching to this advance in physical science. He (the President) looked for brilliant things from the London Radium Institute when it was completed next year. It was imperative before much further work could be done in radium investigation on its physical side to settle once for all the question as to the exact atomic weight of radium. One of the latest authoritative numbers was that of Thorp—226.7—which agreed fairly well with Mme. Curie's estimate.

CORRESPONDENCE.

INTERNATIONAL CONGRESS OF RADIOLOGY
AND ELECTRICITY.

To the Editor of the Chemical News.

SIR,—Arrangements have been made for an International Congress of Radiology and Electricity to take place at Brussels in connection with the Exhibition to be held there in 1910. The Congress will meet on September 6th, 7th, and 8th, and I venture to think that the following details may be of interest to your readers.

The Congress will be held in three sections, and the subjects to be dealt with will include the following:—

In the first section, general questions of terminology and methods of measurement in radio-activity and subjects connected with ions, electrons, and corpuscles will be dealt with.

The second section will be divided into various subsections, dealing respectively with fundamental theories of electricity, study of radiations (including spectroscopy, chemical effects of radiations, and other allied questions), radio-activity, atomic theory, cosmical phenomena (including atmospheric electricity and atmospheric radio-activity).

The third section will be biological, and will be devoted to consideration of the effects of radiations on living organisms. The sections will deal with purely biological questions as well as with the use of various radiations for medical purposes, both for diagnosis and therapeutics.

In order to ensure the success of the Congress, committees have been formed in the various countries which will take part in the Congress, and the following scientists have already consented to act as presidents of the committee in each country:

Prof. Lenard (Germany), Prof. Exner (Austria), Prof. Oëtvös (Hungary), Prof. Castillo (Spain), Prof. Barus (United States), Prof. Langevin (France), Prof. Rutherford (Great Britain), Prof. Blaserna (Italy), Prof. Birkeland (Norway), Prof. Lorentz (Holland), Prof. Ferreira da Silva (Portugal), Prof. Hurmuzescu (Roumania), Prof. Lebedew (Russia), Prof. Arrhenius (Sweden), and Prof. Guye (Switzerland).

I am enclosing a provisional programme of the Congress in case there should be any other point likely to be of interest to your readers.

Communications regarding the Congress should be addressed to Prof. Rutherford, or myself, at the University of Manchester, but anyone wishing to become a member of the Congress should communicate his intention directly to the General Secretary, Dr. J. DANIEL, 1, Rue de la Prévôté, Brussels,—I am, &c.,

W. MAKOWER.

Physical Laboratory,
The University, Manchester,
November 2nd, 1909.

Communications relating to the biological and medical section should be addressed to W. DEANE BUTCHER, Holyrood, Ealing, London, W.

MEETINGS FOR THE WEEK.

WEDNESDAY, 17th.—Microscopical, 8. "Recent and Fossil Foraminifera of the Shore Sands of Selsey Bill, Sussex" (Part IV.), by E. Heron-Allen and A. Earland. (The concluding portion of the Lantern Slides illustrating the series of papers will be exhibited). Royal Society of Arts, 8. Inaugural Address of the 156th Session, "An Imperial Navy," by Sir William H. White, K.C.B., &c.

THURSDAY, 18th.—Chemical, 8.30. "Resolution of Asymmetrical Derivatives of Phosphoric Acid," by B. W. D. Luff and F. S. Kipping. "Configuration of Tropine and γ -Tropine and the Resolution of Atropine," by M. Barrowcliff and F. Tutin. "Stereoisomeric Modifications of $\alpha\beta$ -Dibromobenzyl-acetone," by Miss I. Smedley.

PRELIMINARY ANNOUNCEMENT.

A combined INDEX to the first 100 volumes of the CHEMICAL NEWS is now in course of preparation, and it is proposed to publish the same as soon as possible after the completion of the current (hundredth) volume. If any of our Readers have detected errors or omissions in any of the half yearly Indices, we should deem it a favour if they would draw our attention to the same before the end of this year.

THE CHEMICAL NEWS.

VOL C., No. 2608.

ON CERTAIN RELATIONS BETWEEN BOILING-POINTS.

By J. C. EARL.

THERE appears to be a definite rise in boiling-point produced when the chlorine in an organic compound is replaced by bromine. In the case of one atom of chlorine being replaced by one of bromine, the constant rise produced appears to be about $23-24^{\circ}$ C. (Table I.) The selection is made at random. There are, of course, some exceptions but they are not numerous, and no doubt some cause can be assigned to their divergence from the rule. In the case of compounds in which two atoms of chlorine are replaced by two of bromine, the difference in boiling-points is usually about twice $24 = 48^{\circ}$ C. If three atoms of

RECENT ADVANCES IN OUR KNOWLEDGE OF SILICON AND OF ITS RELATIONS TO ORGANISED STRUCTURES.*

By J. EMERSON REYNOLDS, M.D., Sc.D., F.R.S.

I HAVE placed on the table before you a magnificent natural crystal of the colourless mineral *quartz*, which is the property of the Royal Institution. This is the oxide—dioxide—of the element Silicon, about which I have the honour to address you this evening. This oxide of Silicon is—as you are doubtless well aware—commonly called *Silica*, and is met with in Nature in many conditions, either colourless as in this “rock crystal” or coloured in the black *quartz*, in common *topaz* and *amethyst*, and uncrystalline in *agate* and *flint*.

Not only is Silicon widely diffused in Nature in the many forms of its oxide, but it also constitutes between one-third and one-fourth of the original and non-sedimentary rocks—of which the solid crust of the earth largely consists—in these cases being chemically combined with Oxygen and various metals forming natural *Silicates*. In this diagram we have a necessarily very rough estimate of

TABLE I.

Chlorine compound.	B. p. (°C.).	Bromine compound.	B. p. (°C.).	Difference.
Chlorobenzene	132	Bromobenzene	155	23
Propargyl chloride	65	Propargyl bromide	89	24
Allyl chloride	46	Allyl bromide	71	25
Methyl chloride	-24	Methyl bromide	4.5	28.5
<i>n</i> -Propyl chloride	44	<i>n</i> -Propyl bromide	71	27
<i>n</i> -Butyl chloride	77.5	<i>n</i> -butyl bromide	100.4	22.9
Benzoyl chloride	198	Benzoyl bromide	218	20
<i>o</i> -Chloraniline	207	<i>o</i> -Bromaniline	229	22
<i>m</i> -Chloraniline	230	<i>m</i> -Bromaniline	251	21

TABLE II.

Chlorine compound.	B. p. (°C.).	Bromine compound.	B. p. (°C.).	Diff.	No. of halogen atoms.	Difference per atom.
Methylene dichloride	41	Methylene dibromide	98	57	2	28.5
Ethylene dichloride	84	Ethylene dibromide	131	47	2	23.5
Chloracetol	70	Bromacetol	114	44	2	22
Ethidene dichloride	58	Ethidene dibromide	110	52	2	26
Chloral	97	Bromal	172	75	3	25

chlorine are replaced by three of bromine the difference in boiling-points is about three times $24 = 72^{\circ}$ C. (Table II.). Similar relations are noticed when bromine is replaced by iodine, the constant in this case being about 30.

The difference between the boiling-points of chlorine and bromine is $92.4 = 4 \times 23.1$. By analogy with the foregoing compounds, it would appear that chlorine and bromine contained four atoms in the molecule at the boiling-point. Other interesting conclusions may be drawn assuming the truth of what is apparently a rule.

Can anyone tell me the reason of these relations, and where I can find previous investigations on the subject?

23, Lorne Road, Stroud Green.

Messrs. Baird and Tatlock, Ltd., of Cross Street, Hatton Garden, London, have sent us a copy of their new catalogue, a volume of some 800 pages fully illustrated. The continued advance in chemical and physical apparatus makes it frequently necessary to revise and enlarge the lists, and Messrs. Baird and Tatlock have spared no trouble or expense in making their latest as comprehensive as possible. An entirely new section has been added for physico-chemical apparatus, and apparatus are shown for the analyses of milk, oil, paper, water, &c., and a very complete list of pure chemicals and reagents is included.

the relative proportions in which the chief constituents are present.

The Earth's Crust.

(Approximate Average Composition of Non-sedimentary Rocks).

Oxygen	About 47 per cent.
Silicon	28 "
Aluminium	8 "
Iron	7 "
Calcium and Magnesium	6 "
Alkali metals	4 "

The crust of the earth is in fact a vast assemblage of silicon compounds, and the products of their disintegration under the influence of water and other agents produces the various forms of clay, sand, and chalk which constitute so large a portion of the earth's surface.

The solid crust of the earth is actually known to us for but a very few miles down—thirty at most—our deepest mines being mere scratchings on its surface; but, so far as known, practically all its constituents are fully oxidised, and this is probably true at much greater depths. During æons past oxygen has been absorbed as the earth cooled down, and the product is the crust on which we live (see Note). It is probable that the proportion of oxygen

* A Discourse delivered before the Royal Institution, May 28, 1909

diminishes away from the surface until it disappears almost wholly. What of the deeper depths? Are the comparatively light elements arranged more or less in the order of density? Are we to suppose that silicon and some carbon, aluminium, calcium, the elements chiefly comprising the crust, are those nearer the surface, and iron, copper, and the heavier metals nearer the centre?

(NOTE.—An interesting calculation has been made by Mr. Gerald Stoney, from which it appears that a stratum only 9 feet in depth of the surface of the earth contains as much oxygen as the whole atmosphere. See *Phil. Mag.*, 1899, p. 566).

Until recently we knew little more than that the earth is some 8000 miles in diameter; that its mean density is 5.6—5.7, and that its relatively thin outer skin, or crust, has approximately the composition assigned to it in the diagram. By a very skilful use of earthquake observations, the eminent geologist Mr. Richard D. Oldham has, however, lately given us something like a glimpse within the ball, and concludes from his observations that about five-sixths of the earth's radius includes fairly homogeneous material and that the remaining sixth at the centre consists of substances of much higher density ("Constitution of the Interior of the Earth," *Quarterly Journal of the Geological Society*, 1906, lxii., 456). Assuming this to be even roughly true, we conclude that silicon forms probably as great a proportion of this large mass of the earth—whether in the free state or in the forms of silicides—as it does of the crust.

Having thus magnified the office of the important element of which I wish to speak to you, I shall pass to my next point, which is how the element can be separated from quartz, or other forms of the oxide, for it is never met with unless combined with oxygen in any of the rocks known to us.

I have already mentioned that quartz is a dioxide of the element—in fact it is the only known oxide—hence if we remove this oxygen we should obtain free silicon. This is not a very difficult matter, as it is only necessary to heat a mixture of finely powdered quartz with just the right proportion of metallic magnesium. The metal combines with the oxygen of the quartz, and forms therewith an oxide of magnesium, while silicon remains. If the material be heated in a glass vessel the moment of actual reduction is marked by a bright glow which proceeds throughout the mass. When the product is thrown into diluted acid the magnesium oxide is dissolved and nearly pure silicon is obtained as a soft dark brown powder which is not soluble in the acid. This is not crystalline, but if it be heated in an electric furnace it fuses and on cooling forms the dark crystalline substance on the table, which, as you see, resembles pretty closely the graphitic form of carbon, though its density is rather greater (2.6, graphite being 2.3).

Silicon Analogues of Carbon Compounds.

The points of physical resemblance between silicon and carbon are of small importance compared with the much deeper rooted resemblance in chemical habits which exists between the two elements. This is expressed in the Periodic Table of the elements as in the following diagram:—

Na=23, Mg=24, Al=27, Si=28, P=31, S=32, Cl=35.5
Li=7, Be=9, B=11, C=12, N=14, O=16, F=19

where silicon is represented as the middle term of a period of seven elements of increasing atomic weights, just as carbon is the middle term of the previous period. The fact is these two electro-negative or non-metallic elements play leading parts in the great drama of nature, silicon dominating that which has to do with dead matter, while carbon is the great organ-building and maintaining element of all living things. While each carries on the work to which it is best suited under existing terrestrial conditions, they both go about it in somewhat similar ways, and each one shows tendencies to overstep the border line and perform the other's part. This tendency is for various reasons

much more marked in the case of carbon, but I hope to show you presently that silicon is by no means out of touch with living things, and further that it exhibits capacities which render it a potential element of life under other conditions of our planet, but more especially at a much higher level of temperature.

I do not propose to dwell in much detail on the remarkable parallelism of some silicon and carbon compounds, but must refer shortly to a few of them, and the oxides naturally come first.

I have just stated that we know with certainty only one oxide of silicon, the dioxide SiO_2 . This is analogous to the highest oxide of carbon—the well-known CO_2 which plays so important a part in the lives of animals and plants. This familiar carbon compound is a gas under ordinary conditions, but here is some of it in the form of snow. Alongside of this is a vessel containing some finely divided SiO_2 or silica. They are rather like in appearance but they differ greatly in volatility. The CO_2 snow speedily resumes the gaseous state at ordinary temperature, but silica requires a very high temperature indeed even for fusion; however when heated in an electric furnace the oxide can not only be fused but volatilised. In the fused state it can be fashioned into various shapes, and affords most convenient vessels for many purposes, as they are not liable to crack on sudden heating or cooling, and are not attacked by any acid except hydrofluoric acid.

As the difference between the atomic weights of the elements carbon and silicon is only 16 units, silicon dioxide should not differ in volatility nearly so much as it does from carbon dioxide. This and other considerations lead us to the conclusion that silica as we know it is a molecularly condensed substance represented by the expression $(\text{SiO}_2)_n$, where the value of n is probably at least = 6.

Before leaving the consideration of the simple oxide, I should like to show you the effect of radium emanations on a disc of colourless quartz. This disc has been exposed by Sir William Huggins to radium for a considerable time, and the brownish discoloration about the centre of it is due to the action of the rays. Whether the latter reduce a portion of the oxide and separate a minute film of brown silicon, or merely attack some trace of impurity in the quartz is not yet known. I have to thank Sir William Huggins for allowing me to show you this interesting specimen.

The chemical analogies of CO_2 and SiO_2 are very close in many respects, for both act as acid anhydrides and combine with metallic oxides and form similar salts. On the one hand, we obtain the well-known carbonates, such as common soda crystals, and on the other *silicates*, such as sodium *silicate*. I need scarcely remind you that ordinary window and bottle glass are mixtures of silicates of such metals as calcium and sodium.

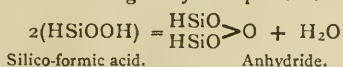
When a soluble carbonate is treated with any moderately strong acid CO_2 gas is evolved; but when a soluble silicate such as Na_2SiO_3 is similarly treated no gas is evolved, but a gelatinous substance separates. Now this consists for the most part of the feeble acid H_2SiO_3 , which parts with the elements of water gradually, if exposed to air, and affords various lower hydrates, one of the most beautiful being that which we meet with in Nature as the precious *opal*.

Chloride and bromide of silicon are easily obtained by heating the free elements in the respective halogens, and precisely correspond in composition to the analogous carbon compounds, but, unlike the latter, are intensely reactive to water, and in so far resemble the chloride and bromide of a metal.

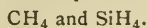
If, however, hydrochloric acid gas, instead of chlorine, be passed over heated silicon, a very volatile liquid is obtained which is similar in composition to ordinary carbon *chloroform*:—

Ordinary chloroform	..	..	..	CHCl_3
Silicon chloroform	..	..	..	SiHCl_3

Silicon chloroform has no anæsthetic effects for a reason you will easily appreciate, when I compare the action of water on the two substances. Under ordinary conditions carbon chloroform is not affected by moisture, hence its vapour can be taken into the lungs unchanged and passes into the system producing its characteristic effects. Silicon chloroform, on the other hand, is instantly destroyed by moisture, producing free acid, therefore it cannot be inhaled. Nevertheless, the products of the action of water upon it at ordinary temperature are very similar to those which can be obtained by the prolonged action of water on ordinary chloroform at high temperatures. The latter can afford formic acid along with hydrochloric acid. Silicon chloroform affords precisely similar products at ordinary temperatures, but the soluble silico-formic acid immediately changes into the anhydride, and that is the white insoluble substance which has separated in the tube before you. This change may be represented thus :—



Again, both silicon and carbon form gaseous compounds with hydrogen of similar composition :—



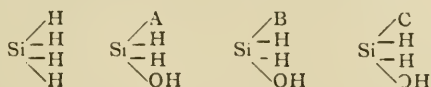
Neither of these hydrides can be obtained by direct union of the respective elements, though they are easily obtained by indirect means, with the details of which I need not trouble you. Both are colourless gases, as you see. The carbon hydride, or marsh gas, is combustible, but requires to have its temperature raised considerably before it takes fire in air, and its flame is only slightly luminous. It produces on complete oxidation water vapour and carbon dioxide gas. The analogous silicon hydride takes fire much more easily in air, and when not quite pure is even spontaneously combustible under ordinary conditions, and it burns producing water vapour and solid silicon dioxide.

"Silico-organic Chemistry."

Now, just as marsh gas may be regarded as the starting point of that great branch of science which is usually spoken of as Organic Chemistry, so the analogous hydride of silicon is the primary compound from which many substances which are often termed silico-organic compounds can be derived by various means, and these were discovered in the course of the classical researches of Friedel, Crafts, Ladenburg, and others.

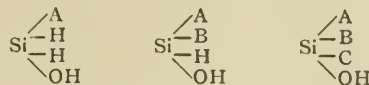
I wish to avoid using many chemical formulæ, which probably would convey but little meaning to some of those whom I address; it will suffice to merely indicate the lines on which investigations have proceeded in this direction.

In the older work of Friedel, Crafts, and Ladenburg, they produced complex substances by the substitution of various radicles (always carbon groups), for one atom of hydrogen in SiH_4 , and ultimately replaced another atom of hydrogen by the OH or hydroxyl group. The substances so formed were silicon *alcohols* which may be represented in the following manner :—A, B, and C, being used to indicate the different complex replacing radicles :—



In this way silicon alcohols were built up which proved to be analogous to well-known carbon alcohols, and which afforded analogous acids, &c., on oxidation. These discoveries laid the foundations of a silico-organic chemistry, and have been further extended in later years. For example, it has been found possible to pursue the analogy with known carbon compounds in the direction of replacing all the hydrogen in silicon hydride by different radicles, and these changes, which can be effected in successive

stages, may be represented in harmony with those just given :—



The two last of these are *asymmetric*, since all four radicles are different. Consequently they should exist in two isomeric modifications, if really analogous to known carbon compounds of the same order, and each form should be capable of acting differently on polarised light (see Note). Dr. F. Stanley Kipping, who has specially investigated this kind of substitution with much success, finds that the analogy between these asymmetric silicon and carbon compounds is complete in regard to optical activity as to other general characters.

(NOTE.—These changes are represented above as having been effected through the silicon alcohols in order to avoid complicating the general statement, other compounds have in fact been found more convenient for the purpose).

Silicon Compounds, including Nitrogen.

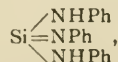
This was all good so far as it went, but some highly important information was still wanting. As you know well, the various compounds, including carbon and *nitrogen*, play by far the most important parts in building up organised structures under the influence of vital energy, but in the silicon series we were almost wholly ignorant of the existence of such compounds until within recent years, when I undertook to definitely investigate this branch of the subject.

All that was known at the period of which I speak was that silicon forms a white nitride of uncertain composition when strongly heated in an atmosphere of nitrogen gas; and that when silicon chloride is brought in contact with ammonia and similar substances violent action occurs, but the nature of the products formed was not known owing to special practical difficulties in separating them.

The first step taken was to examine the action of silicon halides (*i.e.*, chloride, bromide, &c.) on substances free from oxygen, but rich in nitrogen. The earliest of these worked with were thiocarbamides, but in all these cases the silicon halide merely united with the nitrogen compound as a whole, in some instances producing very curious substances, of which the one with allyl-thio-carbamide, $(\text{C}_3\text{H}_5\cdot\text{H}_3\text{N}_2\text{CS})_3\text{SiBr}_4$, is a good example. This is a liquid which flows so slowly at ordinary temperature that it requires nearly a month in order to fall from the top of its containing tube and find its level at the bottom. Several similar substances have been obtained and examined, and their products of decomposition studied, but they do not belong to the class of which I was really in search.

It would weary you to give the details of scientific prospecting which one has to go through in order to attain definite results in a new line of work like this; suffice it to say that success attended the efforts at last, and a finely crystallised and perfectly defined compound was obtained in which silicon is wholly in direct chemical combination with nitrogen, and a specimen of that substance I now show you. Its composition is represented by the expression $\text{Si}(\text{NPh})_4$, where Ph stands for the phenyl group, and its name is silicophenylamide.

This substance when heated undergoes some important changes, which resemble rather closely similar changes that can be effected in analogous compounds of carbon with nitrogen. Thus it first affords a *guanidine*,—



analogous to the well-known carbon guanidine, and, further, a diimide, $\text{Si}(\text{NPh})_2$, which only needs the addition of a molecule of water to convert it into a silicon *urea*, $\text{SiO}(\text{NPh})_2$. Many other substances have been produced

similar to silicophenylamide, and they afford analogous products to these just mentioned; but these have been fully described elsewhere, and need not be dealt with here.

Silicon in Relation to Organised Structures.

The general results of these researches are that we now know a considerable number of silicon compounds including nitrogen, which resemble those of carbon with nitrogen both in composition and in the general nature of the changes in which they can take part. Some of these carbon analogues are closely related to those which are concerned in building up organised structures of plants and animals.

All theories of life assume that its phenomena are inseparably associated with certain complex combinations of the elements carbon, nitrogen, hydrogen, and oxygen, with the occasional aid of sulphur and phosphorus. These are the elements of that protoplasm which is the physical basis of life, and by their interplay they form the unstable and complicated groupings of which that remarkable material is composed. All the phenomena we call vital are associated with the change of some protoplasm, and the oxidation of carbon and hydrogen. But it is quite open to question whether the connection of life with the elements first specified is inevitable. We can conceive the existence of similar groupings of other analogous elements forming other protoplasms capable of existing within much greater ranges of temperature than any plants or animals now known to us have to withstand. For example, we can imagine a high temperature protoplasm in which silicon takes the place of carbon, sulphur of oxygen, and phosphorus of nitrogen, either wholly or in part. In fact, protoplasm so far as we know it in purest form, always contains some sulphur, and often a little phosphorus, representing a very partial substitution of the kind in question.

In view of our newer knowledge there is therefore nothing very far-fetched in supposing that under suitable conditions a plant or an animal organism may be able to construct from silicon compounds, ultimately derived from the soil, something akin to silicon protoplasm for use in its structures.

You will now ask me whether there is any evidence that anything of this kind actually occurs in Nature. I think there is, although I admit that the evidence is not very varied as far as we know.

First, as to the *Vegetable* kingdom. It is well known that many plants take up silicon in some form from the soil, and use it in ways which my botanical friends tell me they do not at present understand. Silicon is present in the straw of cereals, such as wheat, oats, &c., and in most of the *Gramineæ*. It was supposed that the stiffness of the straw was secured by a siliceous varnish, but this view is not now in favour, as it has been found possible to remove silica from the straw by careful treatment, without diminishing its rigidity. It is also present in the leaves of some palms, for my friend Dr. Hugo Müller, in the course of his extensive researches on the sugars present in certain palm leaves, has been much troubled by the presence in the extract from the leaves of siliceous compounds of unknown nature. Again, a well known substance called "Tabasheer," consisting largely of hydrated silica including some organic matter, is obtained at the nodes of some bamboos. What purpose silicon serves in these plants which seem to have special need for it we do not know, but the subject appears to be well worth closer examination than it has yet received at the hands of plant physiologists.

I have on the table some good specimens of Tabasheer, and can show some portions on the screen which have been rendered nearly transparent by soaking in benzene, and under these conditions exhibit traces of structure.

Next, as to the *Animal* kingdom. The most satisfactory evidence that we can at present offer as to the organ-building capacity of silicon comes, curiously enough, from some of the simpler organisms of the animal kingdom, but

the only group the short remaining time at my disposal permits me to notice is that of the *sponges*.

You know that these curious forms of undoubted animal life live in sea-water, and are usually anchored to rocks. The sea contains a very minute proportion of silica in solution, and the sponge has the power of appropriating very considerable quantities in the course of its life, and as a part of its normal food supply. What does it do with this silica? It appears to use it in cell production, and from the cell evolves the beautiful and minute siliceous spicules which are so abundant throughout the structure of many of the sponges.

I have here some photographs of these spicules which I have had taken, and shall throw them on the screen. Two of the best of them have been made from microscopic specimens kindly lent to me by Prof. Dendy, of King's College, London, who has made a special study of these spicules and of their modes of growth.

These structures do not represent mere incrustations, but rather definite growths from the cell protoplasm, and are themselves in the nature of cells of characteristic forms. Prof. Dendy informs me that these spicules in certain cases become surrounded by a horny substance and seem to die, as if by cutting off the supply of energy as well as growing material.

In some of the larger sponges, as in the beautiful *Euplectella aspergillum* or "Venus' Flower Basket," the siliceous material constitutes the greater part of the sponge, as the soft portion resembles a somewhat gelatinous coating from which the exquisite siliceous structure is developed.

To sum up, then, I have shown that silicon can easily take the place of carbon in many nitrogen compounds, as well as in others not including nitrogen. It therefore seems to me that we hazard no very violent hypothesis in supposing that the silicon which enters the sponge in its food, probably as an alkaline silicate, is in the marvellous animal laboratory made to take the place of a portion of the carbon of the protoplasm from which the spicules are ultimately developed.

The hypothesis is at any rate suggestive, and I hope enough has been said to commend it to your consideration, for there seems to be no doubt that silicon is capable of playing a larger part as an "organic element" than we hitherto had reason to suppose.

SOME FORMS OF FOOD ADULTERATION AND SIMPLE METHODS FOR THEIR DETECTION.*

By W. D. BIGELOW Chief of the Division of Foods,
and
BURTON J. HOWARD, Chief of the Microchemical Laboratory.

(Continued from p. 240).

Determination of Artificial Colours.

Detection of Coal-tar Dyes.—As has been stated, colouring matters used with foods are usually soluble in water. If the food under examination be a liquid, it may therefore be treated directly by the method given below. If it be a solid or a pasty substance, soluble in water either in the cold or after heating, it may be dissolved in sufficient water to form a thin liquid. If it contains some insoluble material, it may be treated with sufficient water to dissolve the soluble portion with the formation of a thin liquid and filtered, and then strained through a clean white cotton cloth to separate the insoluble portion. About a half tea-cupful of the liquid thus described is heated to boiling, after adding a few drops of hydrochloric acid and a small piece of white woollen cloth or a few strands of white woollen yarn. (Before using, the wool should be boiled with water containing a little soda, to remove any fat it may contain, and then washed with water). The wool is

* *Bulletin* No. 100, Bureau of Chemistry, U.S. Department of Agriculture.

again washed, first with hot and then with cold water, the water pressed out as completely as possible, and the colour of the fabric noted. If no marked colour is produced, the test may be discontinued and the product considered free from artificial colours. If the fabric is coloured, it may have taken up coal-tar colours, some foreign vegetable colours, and if a fruit product is being examined, some of the natural colouring matter of the fruit. Rinse the fabric in hot water, and then boil for two or three minutes in about one-third of a teacupful of water and two or three teaspoonfuls of household ammonia. Remove and free from as much of the liquid as possible by squeezing or wringing. Usually the fabric will retain the greater part of the natural fruit colour, while the coal-tar colour dissolves in dilute ammonia. The liquid is then stirred with a splinter of wood and hydrochloric acid added, a drop or two at a time, until there is no longer any odour of ammonia. (The atmosphere of the vessel is sometimes charged with the ammonia for several minutes after it has all been driven out of the liquid; therefore one should blow into the dish to remove this air before deciding whether the ammonia odour has been removed or not). When enough acid has been added the liquid has a sour taste, as may be determined by touching the splinter, used in stirring, to the tongue.

A fresh piece of white woollen cloth is boiled in this liquid and thoroughly washed. If this piece of cloth has a distinct colour the food under examination is artificially coloured. The colour used may have been a coal-tar derivative, commonly called an aniline dye, or an artificial colour chemically prepared from some vegetable colour. If of the first class the dyed fabric is usually turned purple or blue by ammonia. In either case if the second fabric has a distinct colour, it is evident that the product under examination is artificially coloured. Of course a dull, faint tint must be disregarded.

Detection of Copper.—The presence of copper, often used to deepen the green tint of imported canned peas, beans, spinach, &c., may be detected as follows:—

Mash some of the sample in a dish with a stiff kitchen spoon. Place a teaspoonful of the pulp in a teacup with three teaspoonfuls of water and add thirty drops of strong hydrochloric acid with a medicine dropper. Set the cup on the stove in a saucepan containing boiling water. Drop a bright iron brad or nail (wire nails are the best and tin carpet tacks will not answer the purpose) into the cup and keep the water in the saucepan boiling for twenty minutes, stirring the contents of the cup frequently with a splinter of wood. Pour out the contents of the cup and examine the nail. If present in an appreciable amount the nail will be heavily plated with copper.

(Caution.)—Be careful not to allow the hydrochloric acid to come in contact with metals, or with the flesh or clothing).

Detection of Turmeric.—In yellow spices, especially mustard and mace, turmeric is often employed. This is especially true of prepared mustard to which a sufficient amount of starch adulterant has been added to materially reduce the natural colour. If turmeric be employed to restore the normal shade an indication of that fact may sometimes be obtained by mixing a half teaspoonful of the sample in a white china dish and mixing with it an equal amount of water, and a few drops (four to ten) of household ammonia, when a marked brown colour, which does not appear in the absence of turmeric, is formed. At the present time turmeric or a solution of curcuma (the colouring matter of turmeric) is sometimes added to adulterated mustard in sufficient amount to materially increase its colour, but not to a sufficient extent to give the brown appearance with ammonia described above. In such cases a teaspoonful of the suspected sample may be thoroughly stirred with a couple of tablespoonfuls of alcohol, the mixture allowed to settle for fifteen minutes or more, and the upper liquid poured off into a clean glass or bottle. To about one tablespoonful of the liquid thus prepared and placed in a small clear dish (a glass salt cellar serves ex-

cellently) add four or five drops of a concentrated solution of boric acid or borax and about ten drops of hydrochloric acid, and mix the solution by stirring with a splinter of wood. A wedge-shaped strip of filter-paper about 2 or 3 inches long, 1 inch wide at the upper end, and one-fourth inch at the lower end, is then suspended by pinning, so that its narrow end is immersed in the solution, and is allowed to stand for a couple of hours. The best results are obtained if the paper is so suspended that air can circulate freely around it, *i.e.*, not allowing it to touch anything except the pin and the liquid in the dish. If turmeric be present a cherry-red colour forms on the filter-paper a short distance below the upper limit to which the liquid is absorbed by the paper, frequently from three-fourths of an inch to an inch above the surface of the liquid itself. A drop of household ammonia changes this red colour to a dark green, almost black. If too much hydrochloric acid is used a dirty brownish colour is produced.

Detection of Caramel.—A solution of caramel is used to colour many substances, such as vinegar and some distilled liquors. To detect it two test-tubes or small bottles of about equal size and shape should be employed, and an equal amount (two or three tablespoonfuls or more) of the suspected sample placed in each. To one of these bottles is added a teaspoonful of fullers' earth, the sample shaken vigorously for two or three minutes, and then filtered through filter-paper, the first portion of the filtered liquid being returned to the filter-paper and the sample finally collected into the test-tube or bottle in which it was originally placed, or a similar one. The filtered liquid is now compared with the untreated sample. If it is markedly lighter in colour it may be taken for granted that the colour of the liquid is due to caramel, which is largely removed by fullers' earth. In applying this test, however, it must be borne in mind that caramel occurs naturally in malt vinegar, being formed in the preparation of the malt. It is evident that the tests require practice and experience before they can be successfully performed. The housewife can use them, but must repeat them frequently in order to become proficient in their use.

(To be continued).

PROCEEDINGS OF SOCIETIES.

THE ROYAL SOCIETY.

Ordinary Meeting, November 4th, 1909.

Sir ARCHIBALD GEIKIE, K.C.B., President, in the Chair.

PAPERS were read as follows, the summaries here printed having been supplied by the authors for use at the Meeting:—

(1) "*The Development of Trypanosoma Gambiense in Glossina palpalis*"; (2) "*A Note on the Occurrence of a Trypanosome in the African Elephant*." By Colonel Sir DAVID BRUCE, C.B., F.R.S., Captains A. E. HAMERTON and H. R. BATEMAN, R.A.M.C., and Captain F. P. MACKIE, I.M.S.

"*On the Perception of the Direction of Sound*." By THE LORD RAYLEIGH, O.M., F.R.S.

"*The Diffraction of Electric Waves*." By Prof. H. M. MACDONALD, F.R.S.

"*On the Mechanism of the Absorption Spectra of Solutions*." By ROBERT HOUSTOUN.

"*Note on the Spontaneous Luminosity of a Uranium Mineral*." By Hon. R. J. STRUTT, F.R.S.

"*The Accumulation of Helium in Geological Time*." II. By Hon. R. J. STRUTT, F.R.S.

The present paper is a continuation of that published in *Proc. Roy. Soc.*, 1908, A, vol. lxxxi., p. 272, the object

being to determine the ratio of helium to radio-active matter in minerals as a means of measuring their age.

The data given refer chiefly to the iron ores of sedimentary strata. Even some of the most recent are found to contain quantities of helium, denoting great antiquity. Thus ironstone from the Eocene beds of Co. Antrim contains, per grm.—

2.64×10^{-4} grs. uranium oxide (U_3O_8),
 8.27×10^{-4} grs. thorium oxide,
 12.1×10^{-4} cc. helium.

This, interpreted according to the best available data, would imply an age of thirty million years.

Experiments of a preliminary character have been made to determine directly the rate of growth of helium in thorianite and in pitchblende. The data thus obtained will give the rate of formation of helium by the complete series of uranium and thorium respectively, and thus to interpret more definitely the results of experiments on other minerals for which a direct determination is not feasible; 400 grms. of thorianite was found to yield in seven weeks a quantity of helium certainly less than 2×10^{-6} cc. The annual rate of production per grm. of thorianite is, therefore, certainly less than 3.7×10^{-8} cc. The 9 cc. initially present cannot, therefore, have accumulated in a less time than 240 million years. An experiment on pitchblende of a similar character was consistent with Rutherford's estimate of the rate of production by the uranium series, but was not on a sufficient scale to afford complete confirmation. Experiments on a larger scale are in progress.

"On the Physical Properties of Gold Leaf at High Temperatures." By J. C. CHAPMAN and H. L. PORTER.

"The Dimensions and Function of the Martian Canals." By Dr. H. C. POCKLINGTON, F.R.S.

The nature of the bed of the canals is guessed from Lowell's value of the velocity of flow along them, and then the depth is calculated from the technical formulae, assuming that the canals are horizontal and carry water from pole to pole. The depth is 500 feet if the canals are as narrow as possible, or 370 feet if they are 4500 feet wide. The amount of water required to fill the canals is determined. To find the function of the canals it is assumed that their arrangement is the most economical, and it is deduced that they are essentially lines of communication, though, of course, they may also serve to carry water for irrigation.

CHEMICAL SOCIETY.

Ordinary Meeting, October 21st, 1909.

Prof. HAROLD B. DIXON, F.R.S., President, in the Chair.

MESSRS. D. F. Blyther and G. J. Woods were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Jehangir Dhanjshaw Anklesaria, Ahmedabad, India; James Alexander Hadden Armstrong, Dumisa, Natal; Donald William Elsom Barker, 2, Hope Street, Wrexham; Harold Baron, B.Sc., 21, Underhill Road, East Dulwich, S.E.; Stanley Robert Best, M.Sc., Hope Villa, Wellington Road, Whalley Range, Manchester; Hubert Frederick Bottomley, The Cedars, Wavertree Road, South Woodford; Henry Shaw Breakpear, B.A., 20, Walton Wood Road, Oxford; Oskar K. H. Burger, Ph.D., 4, Mission Row, Calcutta; Frank Ward Bury, B.Sc., Lyndale Cottage, Darwen; William Edward Callister, B.Sc., The Rowans, Onchan, I.O.M.; William Gordon Carey, Wyngarth, Harpenden; Lakshami Chand, B.A., B.Sc., c/o Messrs. Ramchand and Bulaki Nandan Sahni Street, Benares, U.P., India; James Ferguson Dawson, B.Sc., Glencoe House, Tarbert, Loch Fyne, N.B.; Alfred Charles Dunningham, B.Sc., 28, Victoria Road, Northwich; Edward Charles Edgar, D.Sc., Dalegarth, Romiley, Cheshire; Alfred Edge, Ravenhurst, Clayton Bridge, Man-

chester; Frederick Watson Edwards, 64, Coppice Side, Swadlincote; Arthur James Ewins, B.Sc., 7, Towton Road, West Norwood, S.E.; George Peters Forrester, 69, Beck Strasse, Darmstadt; William Adolf Freymuth, Rangoon, Burma; Otto Fürstenhagen, 28, Schlesische Strasse, Berlin; George Pomeroy Furneaux, B.A., Harbour View, Brixham, S. Devon; Henry Dent Gardner, jun., M.Sc., Fairmead, The Goffs, Eastbourne; Victor John Harding, M.Sc., Lonsdale Terrace, Whitefield, Manchester; Arthur John Harvey, 88a, East India Dock Road, Poplar, E.; Robert Douglas Hendry, 3, Glebe Terrace, Alloa; William Cudmore McCullagh Lewis, M.A., Garmoyle, Bangor, Ireland; Carl Olof Lundholm, 2, Eton Avenue, Hampstead, N.W.; Roland Victor Norris, M.Sc., 1, Howe Street, Higher Broughton, Manchester; Charles Proud, 12, Chancellor Road, Southend-on-Sea; Walter Ritchings, M.Sc., 89, Rosehill Road, Burnley; Pindi Das Sabherwal, Bhera, Punjab; Manindra Sinha, B.A., St. Xavier's College, Calcutta; Spencer Boyd Cortis Stanford, Glenwood, Dalmuir, Dumbartonshire; Guy Stephenson, Alexandra Terrace, Crook, Co. Durham; George Bertram Stones, M.Sc., Bank Villas, Tyldesley, nr. Manchester; James Thallon Strachan, 10, Nelson Street, Sunderland; Hubert Sanderson Tasker, B.A., Emmanuel College, Cambridge; Joseph Grantley Tingle, Nauru, Marshall Islands, Central Pacific; Henry Thomas Tizard, B.A., 23, Geneva Road, Kingston-on-Thames; Herbert Turner, B.Sc., 217, Middleton Street, Moss Side, Manchester; Nikolai Waliaschko, Hohenzollernstr. 12, II., 1, Leipzig; Charles Weizmann, Ph.D., D.Sc., 57, Birchfields Road, Rusholme, Manchester; Herbert Ernest Williams, 70, Wellington Road, Charlton, Kent; Roland Francis Young, c/o Taquah Mining and Exploration Co., Tarkwa, Gold Coast.

Prof. WILLIAM A. TILDEN, D.Sc., F.R.S., then delivered the Mendeléeff Memorial Lecture, at the conclusion of which a vote of thanks was proposed by Sir EDWARD THORPE, C.B., F.R.S., seconded by Sir WILLIAM RAMSAY, K.C.B., F.R.S., and carried by acclamation.

218. "Carthamine." (Preliminary Note). By T. KAMETAKA and ARTHUR GEORGE PERKIN.

Carthamine, the red colouring matter of safflower (*Carthamus tinctoria*), was first isolated by Schlieper (*Annalen*, 1846, lviii., 362) as a red, amorphous powder possessing a cantharides iridescence, and to this he assigned the formula $C_{14}H_{16}O_7$. Radcliffe (*Journ. Soc. Dyers*, 1897, xiii., 158) obtained carthamine from safflower extract as red, iridescent needles melting at $168-169^\circ$ (provisional), but did not analyse this product. The authors corroborate the work of Radcliffe, but regard the compound he prepared as a salt of carthamine, rather than the free colouring matter itself. They find that the crystalline substance is most readily obtained from the extract by means of pyridine and water, but that an elaborate purification is necessary to obtain a pure compound free from calcium, magnesium, and potassium salts. It forms red, iridescent needles, which, when dried at 110° , are exceedingly hygroscopic, and are decomposed at about $228-230^\circ$. Analyses indicate that the formula of carthamine is probably $C_{15}H_{14}O_7$ (Found: C = 58.16; H = 4.87). On fusion with potassium hydroxide, carthamine gives *p*-hydroxybenzoic acid, as stated by Malin (*Annalen*, 1865, cxxxvi., 117), but in the pure condition the dyestuff appears to be much more stable than has been previously suggested.

219. "A Theory Regarding the Configuration of certain Unsaturated Compounds; and its Application to the Metallic Amines and the Cinnamic Acids." By SARAH MARTHA BAKER.

According to the author's theory, if there is sufficient attraction between the other atoms joined to a nitrogen atom and that to which it is doubly bound, there are two possible isomerides, namely, the "en" isomeride, in which the other atoms are grouped round the double bond, and the "ex" or symmetrical isomeride. This theory has been extended to phosphorus, sulphur, and finally, in rare cases, to carbon compounds.

To represent the metallic amines, it is assumed that the ionisable acid groups are connected to the metal through a chain of one or more $\cdot\text{NH}_3\cdot$ groups; but that the non-ionisable acid groups are directly joined to the metal, and, in most cases, prevented from undergoing ionisation by having an NH_3 group also attached, thus: $\cdot\text{M}\cdot\text{X}\cdot\text{NH}_3$. Wherever the grouping $\cdot\text{X}\cdot\text{NH}_3$ occurs there is a possibility of isomerism. An attempt was made to deduce the configuration of the *flavo*- and *croceo*-cobalt salts in terms of this theory.

Applying the same principles to the three cinnamic acids, it was shown that, if ordinary cinnamic acid is represented as "*ex*" fumaroid, isocinnamic acid as "*ex*" maleoid, and allocinnamic acid as "*en*" maleoid cinnamic acid, many of the anomalies in their behaviour are explicable.

220. "*The Relation between the Chemical Constitution of Monoazo-dyes and their Fastness to Light.*" By EDWIN ROY WATSON.

The author puts forward the theory that the fading in light of an azo-dye is due to the oxidation of that part of the molecule which contains hydroxy- or amino-groups, and that the fastness of such a dye is increased by introducing into the phenolic or arylamino-part such other groups as will reduce the tendency to become oxidised.

221. "*The Influence of Gaseous Oxides of Nitrogen on the Rate of Interaction of Chlorine and Hydrogen.*" By DAVID LEONARD CHAPMAN and PATRICK SANSFIELD MACMAHON.

It was shown that the brown gas resulting from the interaction of nitric oxide and chlorine—presumably nitrogen peroxide—inhibits the union of hydrogen and chlorine in the light. The inhibitor is slowly absorbed by the chlorine water in the actinometer, and as it is removed the electrolytic gas gradually recovers its original sensitivity; the removal of the last trace of inhibitor appears to be facilitated by the action of light.

The retardation observed with nitrous oxide was so small that the authors conclude that this gas behaves as a diluent only. In this respect it resembles nitrogen and carbon dioxide.

222. "*Estimation of small Quantities of Ferrous Iron by Potassium Permanganate in the Presence of Hydrogen Chloride.*" By JOHN ALBERT NEWTON FRIEND.

The author has recently shown (*Trans.*, 1909, xcv., 1228) that, if certain precautions are rigidly observed, ferrous iron may be accurately estimated by titration with N/10-potassium permanganate in the presence of any concentration of hydrogen chloride not exceeding $m/4$. Experiments have now been performed in a similar manner with N/25-potassium permanganate and correspondingly smaller quantities of iron. The results are given in the table, the volume titrated being in each case 200 cc. :—

Concentration of hydrogen chloride.	Titr. in cc. KMnO_4 .	Error (cc.).	$\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$.					
			0.5 grm.		1.0 grm.		2.0 grms.	
			Titr. in cc. KMnO_4 .	Error (cc.).	Titr. in cc. KMnO_4 .	Error (cc.).	Titr. in cc. KMnO_4 .	Error (cc.).
$m/20$	23.58	—	23.48	—	23.78	—	23.78	—
$m/8$	23.86	0.28	23.52	0.04	23.79	0.01	23.78	0.00
$m/4$	23.90	0.32	23.57	0.09	23.83	0.05	23.80	0.02
$3m/8$	23.96	0.38	23.60	0.12	23.87	0.09	23.85	0.07
$m/2$	24.12	0.54	23.80	0.32	23.93	0.15	23.88	0.10

The most satisfactory titrations were those obtained in the presence of from 1 to 2 grms. of manganous sulphate, when the concentration of the hydrogen chloride did not exceed $m/4$. In general it was found that 1 grm. of manganous sulphate was preferable to 2 grms., as, in the latter case, the end-point is less permanent, and with larger quantities is fugitive and therefore uncertain. As the presence of manganous sulphate slightly affects the value of the titration of ferrous sulphate in the absence of

hydrogen chloride, it is important to standardise the permanganate with ferrous sulphate in the presence of the same amount of manganous sulphate as will be used in the hydrogen chloride solution.

The chief difficulty is to recognise the end-point, but with a little practice results sufficiently accurate for most purposes can be obtained in daylight, as is evident from a consideration of the above table. Commercial permanganate gave equally good results as the specially pure salt.

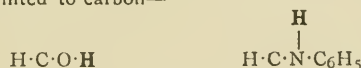
223. "*The Mutarotation of Glucose and its Nitrogen Derivatives.*" By ROBERT GILMOUR.

The author showed that the optical behaviour of the glucosephenylhydrazones (Behrend and Lohr, *Annalen*, 1908, cccxii., 78) brings them into line with glucose-anilide, *p*-toluidide, and other similar compounds which possess the γ -oxidic structure.

On the analogy of the relationship between the specific rotations of the glucoses and the methylglucosides, the value for α -glucose-*p*-toluidide can be calculated ($[\alpha]_D + 226^\circ$), and the calculated value is not widely different from the value found experimentally ($[\alpha]_D + 181^\circ$). The values for α -glucose-*p*-phenetide and β -naphthylamide have been similarly calculated. The fact that tetramethyl glucose-anilide has the rotation $\alpha_D + 224^\circ$ lends support to the idea that α -glucoseanilide has also a high dextrorotation, since it is known that the introduction of four methoxyl groups into the glucose residue has little effect on the optical rotatory power.

It is suggested that the glucosephenylhydrazones possess the γ -oxidic structure, and should thus exist in not more than two stereoisomeric interconvertible forms, having rotations of $\alpha_D + 224^\circ$ and 87° respectively.

The author considers that the mutarotation of glucose and its nitrogen derivatives is due to the presence of a labile hydrogen atom (shown in heavy type) which is not directly united to carbon—



and that the change occurs through the intermediate formation of an unstable aldehydic form. It seems probable that, under ordinary conditions, the γ -oxidic form of glucoseoxime is the more stable; but that under a particular set of conditions, the aldehydic form may be the more stable.

224. "*The Solubility of Bismuth Trisulphide in Alkali Sulphides and of Bismuth Trioxide in Alkali Hydroxides.*" By JOSEPH KNOX.

The author finds that dried precipitated bismuth sulphide dissolves in solutions of both sodium and potassium sulphides, and that the solubility increases rapidly with the concentration of the alkali sulphide. The solubility in potassium sulphide is rather greater than in sodium sulphide of the same concentration. The addition of alkali hydroxides to the alkali sulphide solutions greatly increases the solubility of bismuth sulphide. In a solution of sodium disulphide the solubility of bismuth sulphide is about one-third of that in the corresponding strength of the monosulphide, whilst in solutions of ammonium sulphide and of alkali hydrosulphides and hydroxides, bismuth sulphide is insoluble.

From these facts it is shown that the solubility of bismuth sulphide in alkali sulphide solutions must depend on the formation of a complex anion with the sulphur ion of these solutions.

Bismuth trioxide dissolves to a slight extent in alkali hydroxides, the solubility being approximately proportional to the concentration of the alkali hydroxide. Towards strong bases it therefore behaves as the anhydride of a weak acid, but to a much less extent than the corresponding oxides of arsenic and antimony.

225. "*Substituted Amides of Tartaric Acid.*" By KATE MAUD JACKSON and ALLEN NEVILLE.

The following new substituted amides of tartaric acid

have been obtained, and as some of them illustrate the influence of constitution on the rotatory power of substances, their specific rotations are recorded.

Two determinations of the rotatory power of each substance were made, 1 per cent solutions in pyridine being used:—

	Melting-point.	$[\alpha]_D^{15^\circ}$.	$[M]_D^{15^\circ}$.
Tartarodi-o-anisidide..	180°	155·71	558·25
		155·83	560·78
Tartarodi-p-anisidide..	about 250	205·80	740·88
	(with decomp.)	203·60	732·96
Tartarodi-p-xylylidide..	209	148·87	529·97
		149·61	532·61
Tartarodi-m-4-xylylidide	179	201·16	716·12
		199·98	711·93
Tartarodi-ψ cumidide..	240	168·42	646·73
	(with decomp.)	168·66	647·65

The substances were in all cases prepared from ethyl tartrate, and the amine by heating to about 150° on an oil-bath for several hours. It will be seen that, in the case of the anisidides and xylylidides, as in the case of similar isomeric compounds described by Frankland and Slator (*Trans.*, 1903, lxxiii., 1349), the effect of constitution is very marked. In the case of para- and ortho-compounds, the para has here, as in previously described compounds, the higher rotatory power, whilst in the xylylidides the m-4-compound has a considerably greater rotatory power than the p-compound.

Attempts have been made to prepare similar compounds from the different nitroanilines, but so far without success.

226. "A Volumetric Process for the Estimation of Tungsten." By EDMUND KNECHT and EVA HIBBERT.

The process is based, in the first instance, on the well-known fact that tungstic acid is reduced by zinc and hydrochloric acid to tungsten dioxide, which, in presence of excess of acid, yields a clear light brown solution. If now a solution of a ferric salt be added, the dioxide is oxidised to the trioxide. The end-point is perceived by the disappearance of the intense blue colour of the intermediate compound corresponding with tungsten pentachloride, the reaction $\text{Fe}_2\text{O}_3 + \text{WO}_2 = 2\text{FeO} + \text{WO}_3$ being quantitative. It is thus possible to estimate tungsten volumetrically in presence of iron. Potassium thiocyanate may also serve as indicator, but does not offer any particular advantage.

227. "The Volumetric Estimation of Mercury, and the Estimation of Silver in presence of Mercury." By JOSEPH KNOX.

The thiocyanate method of Rupp and Kraus (*Ber.*, 1902, xxv., 2015) for the estimation of mercury in a solution of mercuric nitrate has been tested, and found to be both rapid and accurate.

The author showed that the estimation of silver by Gay-Lussac's method in presence of mercuric nitrate (by Rupp and Kraus's method) is impracticable, and described a volumetric method which depends on the solubility of silver chloride in potassium cyanide, but the gravimetric estimation of the silver is recommended as being more accurate and convenient. The accuracy of the latter method has been proved in a considerable number of determinations, in which the quantity of mercuric nitrate present was varied greatly.

228. "The Rapid Electro-analytical Deposition and Separation of Metals." Part III. (Preliminary Note). By HENRY JULIUS SALOMON SAND.

A method for the analysis of alloys of copper and tin by electrolysis has been described by A. Fischer (*Zeitsch. Elektrochem.*, 1909, xv., 591), in which an acid tartrate solution is employed in a similar manner as in the copper-bismuth separation given by the author (*Trans.*, 1907, xci., 395). It is stated by Fischer that the tin exerts a retarding influence on the copper, necessitating a higher potential for the complete deposition of the latter than in solutions from which tin is absent. In the experiments now

described, however, no retarding action due to the tin has been observed. The copper may be precipitated completely from boiling solutions at an auxiliary potential of 0·60 volt, just as in the absence of tin. On the other hand, when chlorides are present, these exert a retarding influence varying with the amount of the chloride. This is due to the intermediate production by the current of more or less complex, very slightly dissociated cuprous compounds, which require a high potential for their reduction. The explanation of Fischer's result is to be sought, not in the presence of the tin, but in the fact that it was added by him as stannic ammonium chloride.

The author has separated copper from antimony under similar conditions to those employed for bismuth. The antimony should be present for the greater part in the antimonious state. In the analysis of an alloy, a suitable solution is obtained by employing a hot mixture of dilute nitric and tartaric acids as a solvent, and afterwards neutralising the free mineral acid.

229. "Some Mercury Derivatives of Camphor." By JAMES ERNEST MARSH and ROBERT DE JERSEY FLEMING STRUTHERS.

A detailed description was given of work of which a preliminary account has already appeared (*Proc.*, 1907, xxiii., 246; 1908, xxiv., 267).

230. "The Reduction of Perchlorates by Titanous Salts." By EDMUND KNECHT.

In a recent paper by Rothmund, the reduction of perchlorates by titanous sulphate is discussed, and a method is described for the quantitative estimation of perchlorates, which is based on the complete reduction of the perchlorate by titanous sulphate, followed by the estimation of the resulting chloride by Volhard's process. Rothmund states that it should be possible to effect the estimation of perchlorates by ascertaining, by titration with iron alum, the amount of titanous sulphate that has been oxidised, but no experimental data are given.

Criticising Rothmund's results, Stähler maintains that the latter procedure is liable to give rise to serious errors, since, according to his finding, boiling alone is sufficient to convert some of the titanous into titanic salt.

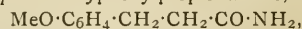
It is now shown that, under suitable conditions, accurate results can be obtained by first reducing the perchlorate with titanous chloride, and then titrating back with standard iron alum, using potassium thiocyanate as indicator. For the successful carrying out of the titration, it is necessary to use the titanous chloride in a concentrated form and to acidify strongly with a mixture of sulphuric and oxalic acids.

231. "Further Syntheses of p-Hydroxyphenylethylamine." By GEORGE BARGER and GEORGE STANLEY WALPOLE.

The isolation of p-hydroxyphenylethylamine, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2$, an active principle of ergot, was recently described (Barger, *Trans.*, 1909, xcv., 1123), together with its preparation by the reduction of p-hydroxyphenylacetone nitrile; two other syntheses have now been carried out.

First, benzoylphenylethylamine, $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NHBz}$, is nitrated, the p-nitro-compound is reduced, the amino-compound converted into the hydroxy-compound by the diazo-reaction, and the benzoyl group is finally removed by heating with acids; instead of the benzoyl, the corresponding acetyl and benzylidene derivatives may be employed.

Secondly, p-methoxyphenylpropionamide,—



is prepared from anisaldehyde; Hofmann's reaction then furnishes p-methoxyphenylethylamine, from which the methyl group is eliminated by heating with acids.

A number of intermediate compounds were also described.

232. "The Constitution of Hydroxyazo-compounds." (Part II.). By WILLIAM BRADSHAW TUCK.

The absorption spectra of the o-hydroxyazo-compounds

and their ethers have been compared with ortho-substituted phenols in which the substituting group contains a double bond in a position analogous to the double bond in the hydroxyazo-compounds. The effect of progressively increasing the degree of unsaturation attached to the azo-benzene nucleus has been investigated. The results obtained confirm the conclusions previously arrived at, and also indicate the reason for the apparently large difference between the absorption spectra of hydroxyazo-compounds and those of their sodium salts.

233. "Optically Active Substances containing no Asymmetric Atom. 1-Methylcyclohexylidene-4-acetic Acid." By WILLIAM HENRY PERKIN, WILLIAM JACKSON POPE, and OTTO WALLACH.

A detailed description was given of work of which a preliminary account has already appeared (*Proc. Chem. Soc.*, xxv., 83).

234. "isoQuinoline Derivatives. Part III. The Oxidation of Substituted 1-Benzyltetrahydroisoquinolines." By FRANK LEE PYMAN.

The results obtained by the oxidation of narcotine, hydrastine, laudanone, N-benzoyltetrahydropapaverine, tetrahydropapaverine, N-ethyltetrahydropapaverine, N-propyltetrahydropapaverine, 1-benzylhydrocotarnine, 1-ethylhydrocotarnine, 1-propylhydrocotarnine, and 1-benzyl-2-methyltetrahydroisoquinoline appear to justify the following general conclusions:—

1. That substituted 1-benzyltetrahydroisoquinolines suffer oxidation and fission simultaneously under the influence of hot dilute sulphuric acid and manganese dioxide, yielding the aldehyde corresponding with the substituted benzyl group, and a basic degradation product.

2. That in the case of substituted 1-benzyl-2-alkyltetrahydroisoquinolines, the basic product is a substituted 2- β -alkylaminoethylbenzaldehyde, which yields salts of the corresponding 2-alkyl-3:4-dihydroisoquinolinium hydroxide.

3. That in the case of substituted 1-benzyl-2-acyltetrahydroisoquinolines, and 1-benzyltetrahydroisoquinolines containing a free imino group, the basic product is a substituted 3:4-dihydroisoquinoline.

4. That substituted 1-alkyltetrahydroisoquinolines do not undergo this type of change.

235. "Contributions to the Theory of Solutions." By JOHN HOLMES and PHILIP JOHN SAGEMAN.

The authors have investigated the changes in volume which occur on mixing methyl iodide with ethyl alcohol, *n*-propyl alcohol, and acetone. The conclusion is drawn that acetone is aggregated in a similar manner to the *n*-primary alcohols, and that methyl iodide possesses twice this complexity; this conclusion receives support from the proportions of methyl iodide in admixture with the lower primary alcohols which exhibit a maximum absorption of heat. Aniline and ethyl acetate are also found to be aggregated similarly to the *n*-primary alcohols.

It is found that the change in volume produced on gradually neutralising a base with an acid is directly proportional to the quantity of salt formed.

The results of the investigation tend to the conclusion that physical forces only are operative in solution, and that theories requiring electrolytic dissociation or combination of solvent with solute are unnecessary for understanding many of the phenomena common to aqueous and non-aqueous mixtures.

236. "The Constitution of Polynitrophenols in Alkaline Solution." By BERTRAM HAWARD BUTTLE and JOHN THEODORE HEWITT.

The absorption spectra of 2:4- and 2:6-dinitrophenols in acid and alkaline solution have been examined, and whilst the latter gives solutions showing absorptions similar to those of *o*-nitrophenol, solutions of the 2:4-isomeride show more resemblance to *p*-nitrophenol. The conclusion is thus drawn that 2:4-dinitrophenol gives para- rather than ortho-quinonoid salts.

Picric acid, being a very strong acid, is nearly com-

pletely ionised in dilute aqueous solution, the absorption spectrum produced by an aqueous solution of the acid being practically identical with that of the sodium salt, but differs very markedly from that given by 2:4:6-trinitroanisole.

Attention was drawn to the influence exerted on nitro-groups attached to aromatic nuclei by other nitro-groups in the meta-position.

237. "The Preparation of Disulphides. Part VII. The Nitrobenzyl Mercaptans and Disulphides." By THOMAS SLATER PRICE and DOUGLAS FRANK TWISS.

By the hydrolysis of the three sodium alkyl thiosulphate compounds, the corresponding *o*-, *m*-, and *p*-nitrobenzyl mercaptans have been prepared. By oxidation with iodine the corresponding disulphides were obtained. The properties of the disulphides prepared in this way agree with those of the compounds obtained by the action of alkali on the sodium nitrobenzyl thiosulphates (*Trans.*, 1908, xciii., 1402).

The method of preparation of *p*-nitrobenzyl disulphide given by Strakosch (*Ber.*, 1872, v., 692) was investigated, and shown to yield a mixture of the monosulphide, disulphide, and mercaptan. The substance described by Strakosch as the disulphide appears to have been a mixture of disulphide and mercaptan, and the compound described by him as the mercaptan was really the impure monosulphide.

The melting-points of the nitrobenzyl mercaptans are:—Ortho, 29.5°; meta, 14°; and para, 52.5°. These are slightly different from those given by previous observers, the discrepancies being probably due to traces of disulphide in the mercaptans previously obtained.

Gutmann's recent results (*Ber.*, 1909, xlii., 228) on the action of acids on sodium and potassium ethyl thiosulphates were discussed, and shown to be in accordance with the usually accepted constitutional formula for sodium thiosulphate.

238. "A Colorimetric Method for the Estimation of Small Quantities of Vanadium." By ARNOLD WILLIAM GREGORY.

The method is based on the colour reaction which takes place when a solution of vanadium in concentrated sulphuric acid is added to a solution of strychnine in the same acid. A violet colour is first formed, and this changes to orange. As the latter colour is quite permanent, and is proportional to the quantity of vanadium present, a comparison of the colour produced with that given by a known amount of vanadium under similar conditions indicates the amount of vanadium present in the solution tested. This test is not given by titanium, tungsten, or molybdenum, nor does their presence in relatively large quantities interfere with the formation of the colour given by vanadium. The presence of iron interferes with the reaction. This element must therefore be removed before the test can be applied.

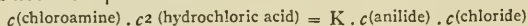
239. "Chlorination and Bromination of Acylanilides. A Direct Process." (Preliminary Note). By KENNEDY JOSEPH PREVITÉ ORTON and WILLIAM JACOB JONES.

In the chlorination (or bromination) of acylanilides, the chloroamines, Ar·NCl·Ac, are not intermediate steps, in the sense that they are first formed, and then change by an intramolecular rearrangement into the chloroacylanilides. The substitution of hydrogen in the benzene nucleus of anilides is rather the result of a direct interaction of chlorine (or bromine) and anilide. In the conversion of a chloroamine into the isomeric anilide under the influence of hydrochloric acid, the presence of which is essential, the chloroamine first reacts with hydrochloric acid, thus: Ar·NCl·Ac + HCl $\rightleftharpoons$ Ar·NH·Ac + Cl₂ (Orton and Jones, *Trans.*, 1909, xcv., 1456); then the free chlorine and the anilide interact.

Among the mass of evidence which the authors have accumulated in favour of the above statement, the following will serve as an illustration. In a solution of acetylchloroamino-*p*-chlorobenzene and hydrochloric acid (concentration of each = 0.025 grm.-molecules per litre) in 50 per cent acetic acid, in which about 1.2 per cent of the total chlorine

is free, the formation of 2:4-dichloroacetanilide is about twice as rapid as the formation of *p*-(and *o*-)chloroacetanilide in a similar equimolecular system composed of acetylchloroaminobenzene and hydrochloric acid, in which only a trace of free chlorine is found. Yet in a system composed of acetylchloroamino-*p*-chlorobenzene, acetanilide, and hydrochloric acid in the same medium, the acetanilide only is chlorinated; *o*- and *p*-chloroacetanilides are formed, but no 2:4-dichloroacetanilide. The speed of the change is about six times that of the system composed of acetylchloroaminobenzene and hydrochloric acid. On the assumption that the formation of the monochloroacetanilides is from the chlorine (set free from the acetylchloroamino-*p*-chlorobenzene) and acetanilide and not through the chloroamine of acetanilide, it should follow, since no 2:4-dichloroacetanilide is produced, that the rate of interaction of chlorine and acetanilide is very large relative to that of chlorine and *p*-chloroacetanilide. Comparative measurements made in glacial acetic acid, where only chlorine and anilide but no chloroamine are present (*loc. cit.*), show that the chlorination of acetanilide is about 160 times as speedy as that of *p*-chloroacetanilide.

From this view of the process of chlorination, it follows that the velocity is given by $k \cdot c(\text{anilide}) \cdot c(\text{chlorine})$; but since the equilibrium—



holds (Orton and Jones, *loc. cit.*), the velocity equals $k \cdot c(\text{chloroamine}) \cdot c_2(\text{hydrochloric acid})/K$. Since the concentration of hydrochloric acid remains constant during the conversion of the chloroamine into a chloroanilide, the velocity of conversion in a system in which the proportion of chlorine and anilide is small (dilute acetic acid) is proportional to the original concentration (*C*) of the chloroamine, and = $k \cdot C(\text{chloroamine}) \cdot \text{Const.}/K$; that is, the reaction is apparently unimolecular. When the proportion of chlorine and anilide is small, and at the same time the hydrochloric acid, the concentration of which is varied, is in excess, the speed of the transformation is approximately proportional to the square of the concentration of the hydrochloric acid used in the system. In Blanksma's observations on the transformation of acetylchloroaminobenzene, in which a considerable excess of hydrochloric acid was used, the reaction was found to be apparently unimolecular, and the speed proportional to the square of the concentration of the hydrochloric acid. When the above limitations are not imposed, the present measurements show that the reaction is not apparently unimolecular and the speed is not approximately proportional to the square of the concentration of the hydrochloric acid, but is in accord with the proposition laid down in the foregoing.

When chlorine and an anilide interact, two changes occur, namely, the formation of a C-chloro-derivative, an irreversible change, and the formation of an N-chloro-derivative, a reversible change. With the great majority of anilides, when the acetic acid medium is sufficiently dilute, the latter reaction is the more rapid; the equilibrium above mentioned is attained, which is only slowly displaced by the formation of the C-chloro-derivative. In the case of acetanilide, however, chlorination in the nucleus is faster than in the imino-group.

It is suggested that the peculiar influences of amino-, imino-, and hydroxy-groups on substitution in the benzene nucleus are largely due to the possibility which their presence offers of the transient formation of highly reactive *o*- and *p*-quinonoid phases of the benzene nucleus.

240. "The Benzyl and Nitrobenzyl Selenosulphates and the Benzyl and Nitrobenzyl Diselenides." By THOMAS SLATER PRICE and LIONEL MANFRED JONES.

In a preliminary note (*Proc.*, 1908, xxiv., 134) the preparation of benzyl diselenide from sodium selenosulphate and benzyl chloride has been described. An attempt to extend this method of preparation to the nitrobenzyl diselenides was not successful until the sodium selenosulphate was replaced by the potassium salt.

The diselenides were prepared from the alkyl selenosul-

phates either by the action of iodine or by electrolysis in a divided cell after potassium hydrogen carbonate had been added to the solution (compare Price and Twiss, *Trans.*, 1907, xci., 2021). The iodine method was the most general one, the reaction taking place quantitatively at the ordinary temperature, according to the equation $2\text{KO} \cdot \text{SO}_2\text{SeR} + 2\text{H}_2\text{O} + \text{I}_2 = \text{R}_2\text{Se}_2 + 2\text{KHSO}_4 + 2\text{HI}$. This reaction was made use of in the analysis of the selenosulphates. Benzyl and also the *p*- and *m*-nitrobenzyl diselenides could be prepared by the electrolytic method, but not the corresponding ortho-compound.

The potassium benzyl and nitrobenzyl selenosulphates are all crystalline compounds, which are fairly readily soluble in water; the solutions give no precipitate with barium chloride. The *p*-nitrobenzyl compound possesses a slight creamy tinge, the others being colourless.

The diselenides are all more or less yellow crystalline compounds, their melting-points being:—Benzyl, 92–93°; nitrobenzyl: ortho, 103.5°; meta, 106°; para, 107.5°.

Both the selenosulphates and the diselenides undergo decomposition with liberation of selenium on exposure to diffused daylight. The benzyl compounds are the least stable, turning red in a few hours. Exposure of one or more days is necessary to affect the nitrobenzyl compounds, the meta being the most stable.

241. "The Action of Ammonia on the Glycide Aryl Ethers. Part I. *o*-Tolylxypropanolamines." By DAVID RUNCIMAN BOYD and (in part) HERBERT S. KNOWLTON.

Glycide *o*-tolyl ether, $\text{O} \begin{array}{l} \text{CH} \cdot \text{CH}_2 \cdot \text{O} \cdot \text{C}_7\text{H}_7 \\ | \\ \text{CH}_2 \end{array}$, an oil

boiling at 134.5°/14 mm., has been prepared, and the action of aqueous ammonia on it has been investigated.

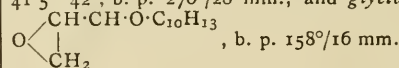
Three bases have been isolated, namely, β -amino- β' -*o*-tolylxyisopropyl alcohol, $\text{C}_{10}\text{H}_{13}\text{O}_2\text{NH}_2$, m. p. 58–60°, b. p. 177°/11 mm.; dihydroxy-di-*o*-tolylxydipropylamine, $\text{C}_{10}\text{H}_{13}\text{O}_2\text{NH}$, m. p. 117.5°; and trihydroxy-tri-*o*-tolylxytripropylamine, $(\text{C}_{10}\text{H}_{13}\text{O}_2)_3\text{N}$, m. p. 83–84°.

Various derivatives of these bases were described.

242. "The Action of Potassium Hydroxide on Epichlorohydrin in presence of Monohydric Phenols." By DAVID RUNCIMAN BOYD and ERNEST ROBERT MARLE.

A criticism of Zunino's paper (*Atti R. Accad. Lincei*, 1909, [5], xviii., I., 254).

The following new compounds were described:—Glycerol dithymyl ether, $\text{OH} \cdot \text{CH}(\text{CH}_2 \cdot \text{O} \cdot \text{C}_{10}\text{H}_{13})_2$, m. p. 41.5–42°, b. p. 270°/28 mm., and glycide thymyl ether,

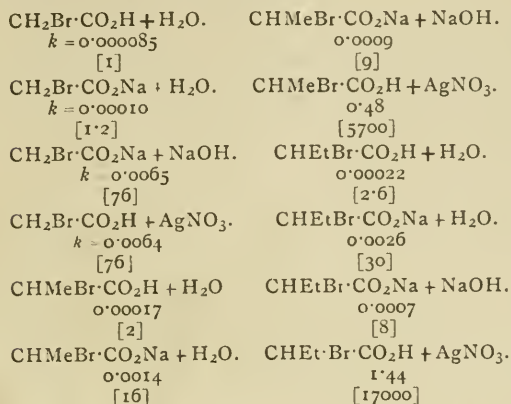


243. "Reactivity of the Halogens in Organic Compounds. Part III. Interaction of Bromoacetic, α -Bromopropionic, and α -Bromobutyric Acids, and their Sodium Salts with Water and with Alkali." By GEORGE SENTER.

The results of the velocity measurements are summarised in the accompanying table, in which *k* in each case represents the initial velocity, in N/10-solution at 52.4°, of the reaction represented by the equation below which it is placed. The numbers in brackets give the relative initial velocities of the reactions under equivalent conditions, referred to the slowest—the reaction between bromoacetic acid and water—as unity.

As regards the mechanism of the chemical changes, the main reaction for those of the first type probably takes place between non-ionised acid and non-ionised water. In the case of the sodium salts and water, the experimental results are best accounted for on the assumption that the anion loses a bromine atom along with the negative electron, thus, $\text{R} \cdot \text{CHBr} \cdot \text{COO}' \rightarrow \text{R} \cdot \text{CH} \cdot \text{COO}' + \text{Br}'$, the residue immediately uniting with water to form the hydroxy-acid. The main reaction with the sodium salts and sodium hydroxide takes place between the anions $\text{R} \cdot \text{CHBr} \cdot \text{COO}'$ (where R represents hydrogen or an alkyl group) and OH' ions. The comparatively slow reaction between these ions (as contrasted with the rapidity of ester

hydrolysis) is probably due to repulsion between the negative charges on the two groups. The results with silver nitrate are provisional, and these reactions will be discussed in a later communication.



244. "Ethyl Ether. Part I. The Influence of Water and Alcohol on its Boiling-point." By JOHN WADE and HORACE FINNEMORE.

Ether as usually purified is not homogeneous, and is resolvable into two physical constituents by accurate fractionation. The more volatile constituent contains water that has escaped the ordinary drying agents, and under suitable conditions may be isolated as a binary mixture of ether and water, having a constant and minimum boiling-point, 34.15° (corr.), and containing about 1.3 per cent of water. At the ordinary temperature this binary mixture is practically a saturated solution of water in ether; it has been found incidentally that the solubility of water is approximately constant at 0.013 grm. per grm. of ether between 20° and 15° , and then decreases to 0.009 grm. per grm. at 10° , the lowest temperature examined.

The less volatile constituent obtained on fractionating ordinary ether is approximately pure ether, b. p. 34.50° (corr.). In presence of alcohol the boiling-point may be appreciably raised, by an amount varying with the proportion of alcohol in the still; the highest observed was 34.73° (corr.). There is no evidence, however, of the formation of a definite physical mixture, for although a very appreciable amount of alcohol passes over with the ether, this may be gradually eliminated by repeated fractionation. Alcohol has a similar influence on the boiling-point of the binary aqueous mixture, and when ether containing both water and alcohol is fractionated, indications of a third physical constituent are sometimes obtained. This, however, is not due to the formation of a binary mixture of ether and alcohol, nor to that of a ternary mixture of all three substances, but is probably caused by the elevation in the boiling-point of the binary aqueous mixture as the concentration of the alcohol increases.

The mutually opposing influences of water and alcohol on the boiling-point of ether render constancy of its boiling-point as determined in the ordinary manner useless as a criterion of purity.

245. "A Method for the Measurement of Vapour Pressures." By ALEXANDER CHARLES CUMMING.

A solution of hydrate is kept at constant temperature in an evacuated glass vessel, and the vapour tension measured by a dew-point method. In the apparatus described, a silver cylinder is cooled slowly, and the temperature noted at which dew appears on the silver surface. The corresponding vapour pressure is then obtained by reference to a table of vapour pressures of the pure solvent. With attention to certain details, the method was found to be convenient and accurate. The vapour pressures of different concentrations of sulphuric acid at various tem-

peratures were determined, and the results were found to be in good accord with the values given by Regnault and by Sorel. A few measurements of the vapour tensions of salt hydrates were also made. The method has the marked advantage over the differential tensimeter method that no error is introduced by small amounts of residual air in the apparatus.

SOCIETY OF CHEMICAL INDUSTRY.

Ordinary Meeting, November 1st, 1909.

Dr. LEWKOWITSCH in the Chair.

"Technical Gas Calorimetry." By J. H. COSTE.

The steadily increasing use of gaseous fuel and the introduction of the incandescent gas mantle have rendered the determination of calorific power of gas a matter of considerable importance.

The researches of Thomson and Berthelot have made it possible for the calorific power of gaseous mixtures to be calculated from their composition with a fair degree of accuracy. The assumption that the calorific power of the unsaturated hydrocarbons is equal to that of propylene, i.e., 551 nett calories per cubic foot, gives results which agree well with direct determinations.

For most purposes it is more convenient to use a direct rather than an indirect method of determining the calorific power of gas. Calorimeters of two types are considered. For the determination of the calorific value of a gas supply flow calorimeters are more suitable than those of the still water type. The sources of error incident to such calorimeters as Junker's and Boys's and the nature and magnitude of the corrections required are indicated. The agreement of the results obtained with these two instruments is shown.

The relations between calorific power and method of manufacture and between calorific and illuminating power are discussed. The points raised are illustrated by tables and records of experimental work.

"On Naphthalene Picrate and the Quantitative Determination of Naphthalene." By W. P. JORISSEN and J. RUTTEN.

The authors refer to the fact that in the Colman-Smith method for the determination of naphthalene too low results are invariably found. The authors point out that Rutten obtained accurate results by making use of a saturated solution of picric acid. A description of the method is given together with the results of some analyses. An explanation for the more favourable working of the concentrated solution is afforded by the application of the phase rule. The authors verify their conclusions by an extended series of experiments on the solubilities of picric acid, naphthalene, and naphthalene picrate.

Attention is called to the decomposition of naphthalene picrate in aqueous acetic acid and benzene solutions, and particulars are given of experiments on the boiling-point of an alcoholic solution of the picrate. The new facts furnish an explanation of previously observed discrepancies in the determination of naphthalene.

"Some Notes upon the Manufacture of large Blocks of Artificial Stone from Sand and Lime." By T. C. STEAD.

The author dealt especially with large blocks of artificial stone made from a mixture of silica and quicklime fed into moulds by suitable filling apparatus, and gave particulars of work with different proportions of materials, varying sizes of blocks, and the effect of weather upon the stone.

The conclusions arrived at were that mixtures containing lime below a certain percentage resulted in a stone of insufficient strength, which cracked during or immediately after its formation, and was unduly porous and friable.

An increase in the quantity of lime gave a stone sufficiently hard and sound, provided that the whole of the mass were uniformly saturated with water in the first instance. This uniformity of saturation is not always easy of attainment, and the lack of it gave rise to non-homo-

geneous and cracked blocks. Uniformity of materials and working produced uniform results. Varying temperatures, however, seriously affected newly made stone otherwise without faults. Sound stone which was not subjected immediately after making to varying conditions of climate stood well, but low temperatures and bad weather adversely affected it and made some period of seasoning in a suitable atmosphere necessary.

NOTICES OF BOOKS.

The Evolution of the Sciences. By L. HOULLEVIGUE.
Translated from the French. London and Leipzig: T. Fisher Unwin. 1909.

EVERY one of the nine essays which this book contains exhibits to a marked degree the author's power of summarising the extent of men's knowledge of natural science, and at the same time they show how he can make the problems of each branch clear and the true value of advances in all directions apparent. He is bound by no dogmatic tendencies nor held back by any sort of conservatism, but expresses in very lucid language views which sometimes appear ahead of the times, writing for the earnest student and for the growing class of men who believe that progress in science is the only true and useful progress. He points out and emphasises the dangers of over specialisation, which tends to narrowness and incompleteness of thought. The first essay deals with the tendencies of modern chemistry, and the loss of absolutism by the laws enunciated since the birth of modern chemistry, and in the second essay the experiments of Ramsay, which indicate that the great law of the fixed and unalterable nature of each of the elements is tottering, are discussed more fully. The author has made this chapter particularly interesting, and the student will find something to ponder over in each paragraph. Essays on the existence of matter and the condition of the interior of the earth follow, while in a chapter on the sun the methods and results of the examination of the sun's surface are described. These more astronomical subjects (though the author, by the way, would have us classify sciences not according to the present day system but as sciences of the ether, sciences of inanimate matter, and sciences of life) include the structure of the Milky Way and eclipses. In the eighth essay the famous experiments on the origin of life, or rather the part played by physical and chemical forces in the growth of the organism, are described; and the last, which is perhaps the most inspiring of all, deals with those enchanting regions common to many sciences, the frontier lands which are awaiting exploration, and which offer the prospect of definite advances of knowledge even more than the highly specialised examination of the details and minutiae of one science, be it chemistry, physics, or biology.

The Vegetable Proteins. By THOMAS B. OSBORNE, Ph.D.
London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1909.

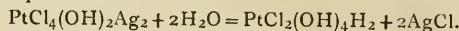
IN this monograph the author has aimed at giving a general account of the chemical and physical properties of the vegetable proteins rather than discussing the characteristics of individual members of this class of substances. Hence only general methods of isolation are described, and tables showing the physical constants of the most important vegetable proteins are included. The decomposition of the proteins under the action of different reagents is discussed fairly fully, and summaries of much of the author's own work are included, so that the monograph is considerably more than a mere compilation. The author's suggestion of the name "protean" for the insoluble substances obtained from seed proteins seems suitable, and the formation of a protean is apparently a characteristic general reaction of all vegetable proteins. The scheme of classification suggested by the American Committee is explained in some detail as being on the whole the most satisfactory system.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlix., No. 14, October 4, 1909.

Examination of Essence of Terebenthene.—Paul Nicolardot and Louis Clément.—Essence of terebenthene may be old, badly prepared, or adulterated. In the first case the essences are strongly acid, and an acid reaction does not show that the essence is adulterated. Essences oxidise in the light and become acid even in dry vessels. Adulterated essences are only slightly acid, and contain petrol (light oils, white spirit, &c.). The presence of petrol derivatives is shown by an increase in the rotatory power, and that of resin oil by a decrease; petrol lowers the flash-point, and white spirit does not affect it, while oil of resin raises it.

Decomposition of Argentic Tetrachloroplatinate by Water and Preparation of Fulminating Platinum.—Jules Jacobsen.—Argentic tetrachloroplatinate is decomposed by boiling with water, bichloroplatinic acid being formed, and silver chloride mixed with a platinum compound less rich in chlorine than the tetrachloroplatinate. The equation is—



The yield of bichloroplatinic acid is 80 or 90 per cent. With excess of ammonia bichloroplatinic acid gives a brown flocculent precipitate which blackens when heated and then explodes violently, the products being platinum black, nitrogen, oxygen, and water vapour. The formula of the compound appears to be $(\text{OH})_5\text{PtNH}_3\text{Pt}(\text{OH})_5$. With pyridine bichloroplatinic acid gives the corresponding compound $(\text{OH})_5\text{PtC}_5\text{H}_5\text{NPt}(\text{OH})_5$, which also explodes on heating.

OBITUARY.

DEATH OF DR. W. J. RUSSELL, F.R.S.

IT is with much regret that we announce the death of Dr. W. J. Russell, F.R.S., which occurred on November 12th. We hope to publish an obituary notice of his career in our next issue.

MISCELLANEOUS.

Chemical Society Research Fund.—A meeting of the Research Fund Committee will be held in December next. Applications for Grants, to be made on forms which can be obtained from the Assistant Secretary, must be received on, or before, Monday, December 6th, 1909. All persons who received grants in December, 1908, or in December of any previous year, whose accounts have not been declared closed by the Council, are reminded that reports must be in the hands of the Hon. Secretaries not later than Wednesday, December 1st. The Council wish to draw attention to the fact that the income arising from the donation of the Worshipful Company of Goldsmiths is to be more or less especially devoted to the encouragement of research in inorganic and metallurgical chemistry. Furthermore, that the income due to the sum accruing from the Perkin Memorial Fund is to be applied to investigations relating to problems connected with the coal-tar and allied industries.

MEETINGS FOR THE WEEK.

WEDNESDAY, 24th.—Royal Society of Arts, 8. "Photo-telegraphy" (with Practical Demonstrations), by T. Thorne Baker.

FRIDAY, 26th.—Physical, 5. "Effective Resistance and Inductance of Helical Coil," by J. W. Nicholson. "Ductile Materials under Combined Stress," by W. A. Scoble. "Recoil of Radium C from Radium B," by W. Makower and S. Russ. "The Sun's Motion with respect to the Ether," by C. V. Burton.

THE CHEMICAL NEWS.

VOL C., No. 2609.

A NEW RAPID VOLUMETRIC METHOD FOR THE DETERMINATION OF NIOBIUM IN THE PRESENCE OF TANTALUM, AND ITS APPLICATION TO THE ANALYSIS OF NIOBIUM MINERALS.*

By F. J. METZGER and C. E. TAYLOR.

THE determination of niobium and tantalum, when existing together, has always been a stumbling block to the analytical chemist. The only method at present available is one based on the fractional crystallisation of the double fluorides of these elements with potassium. The results by this method at best can be only approximate, as may be understood when the relative solubilities of these two double salts are considered. The solubility of the double potassium tantalum fluoride being given as one part of salt in 200 parts of water, whereas the corresponding niobium salt is soluble one part in 12.5 parts of water. Although with considerable experience and care duplicate analyses may be made by the crystallisation method which show agreement, within about 1 per cent, or even less, the values obtained do not represent the actual amounts of the elements present, as is reasonable to be supposed from the solubilities given above.

Osborne (*Am. Journ. Sci.*, 1885, xxx., 328) describes a method for the determination of niobium and tantalum in the presence of titanium, which involves the reduction of the hydrochloric acid solution (containing a small amount of fluorides) of the combined elements, titration of the niobium and titanium, determination of the titanium colorimetrically, the tantalum being found by difference. But one determination is reported, which was made on a known mixture of oxides.

Warren (*CHEMICAL NEWS*, 1906, xciv., 298) found the method of Osborne to be very inaccurate.

After a great deal of preliminary experimentation, it was found that, if succinic acid was added to a solution of niobium and tantalum in strong sulphuric acid, the solution could then be largely diluted, also heated, without precipitation of either the niobium or tantalum. This fact formed the basis of the work which follows.

Experimental.

Inasmuch as succinic acid is not affected by potassium permanganate in acid solution, it was thought that the niobium might be reduced by zinc and acid, and then titration made with potassium permanganate, and that the tantalum should remain unaffected by either operation.

Material.—The material used in this work was prepared from South Dakota columbite, the niobium and tantalum freed from impurities by the usual method, then subjected to many recrystallisations, finally obtaining niobium and tantalum double fluorides of a high degree of purity.

Preliminary experiments showed that the niobium could readily be reduced when in sulphuric acid solution containing succinic acid, and could then be titrated by means of potassium permanganate solution, and that the presence of tantalum did not interfere.

Standardisation of Solution.—The first experiments were made to determine the potassium permanganate standard in terms of Nb_2O_5 . The experiments were made as follows:—

About 0.2 gm. of Nb_2O_5 was fused with potassium bisulphate, the fusion treated with 40 cc. of concentrated sulphuric acid by adding part of the acid to the crucible, heating to a clear solution, transferring the solution to a beaker, and cleaning the crucible by washing with the

remainder of the acid. Six grms. of succinic acid were then added to this concentrated sulphuric acid solution, which was then diluted somewhat with a saturated aqueous solution of succinic acid, and water added to a volume of 200 cc., and while still quite warm (from dilution) passed through the reductor, followed by 200 cc. of about 5 per cent sulphuric acid, and titrated immediately with potassium permanganate solution.

Results are given in terms of Nb_2O_5 per cc. of potassium permanganate solution used, and also, in the last column, the values converted to terms of exactly $N/10KMnO_4$, as shown in Table I.

The reductor used was 19 inches in length by $\frac{3}{4}$ inch in diameter, and was filled with amalgamated zinc.

A blank experiment containing sulphuric acid and succinic acid was made, and the deduction (0.1 cc.) allowed.

At this point a different potassium permanganate solution was employed as well as a freshly amalgamated lot of zinc.

Zinc considerably Amalgamated.—Temperature $75^\circ C.$, 3 grms. of sodium bicarbonate in the flask. Titrations were made as shown in Table II.

In 10 to 12, inclusive, the solution was passed through the reductor at a boiling temperature instead of at $75^\circ C.$

These results, although very irregular, are considerably higher than have been obtained previously; that is, the reduction was less complete. It was further noticed that the reductor in the experiments, 6 to 13, was less active than in the previous experiments, and it was assumed that the degree of amalgamation of the zinc might be of some significance.

Slightly Amalgamated Zinc.—Less mercury (the amount, however, not being weighed) was used in amalgamating the zinc employed in the experiments of Table III.

These results show greater reduction of the niobium than any previously obtained, due, undoubtedly, to the fact that less mercury was used in the amalgamation of the zinc.

In Experiments 19 and 20 an atmosphere of hydrogen was maintained throughout the reduction and titration. In Experiments 20 and 22, as well as all experiments to follow, an atmosphere of carbon dioxide was maintained throughout the reduction and titration, employing a Kipp generator for carbon dioxide and a long-stemmed burette for the titrations.

Unamalgamated Zinc.—In view of the more complete reduction shown in Table III., where slightly amalgamated zinc was used, it was thought that perhaps there might be some advantage in the use of unamalgamated zinc in the reductor. Experiments were therefore made, filling the reductor with 20 to 30 mesh C.P. zinc, unamalgamated, but the action of dilute sulphuric acid was so very vigorous that the solution could not be drawn through the reductor sufficiently rapidly to prevent stoppage due to the matting together of the fine particles of zinc.

Conditions Adopted for Amalgamation.—It was now believed that, by adopting well-defined conditions for the amalgamation of the zinc, uniformity of results might be obtained, and that these results would be more constant when the zinc is amalgamated only slightly.

The amalgamation of the zinc used in all experiments which follow was carried out in detail as described below.

600 grms. of 20 to 30 mesh C.P. zinc was amalgamated with a solution made by dissolving 0.5 gm. of mercury in 25 cc. of concentrated nitric acid, and diluting to 250 cc. with water. The zinc was shaken in this solution for several minutes, washed with water, then with dilute sulphuric acid, and kept under water until required for use in the reductor. The deduction for a blank on this zinc was 0.1 cc. $KMnO_4$ solution.

Pure Oxides.—The supply of pure Nb_2O_5 having become exhausted, a new lot of material was prepared by taking two different samples of niobium salt and separating each of these into three fractions, which are designated in the table following as I_1 , I_2 , I_3 , and II_1 , II_2 , II_3 .

* From the *School of Mines Quarterly*, xxx., No. 4.

TABLE I.

No.	Nb ₂ O ₅ taken.	Time, minutes.	KMnO ₄ , required cc.	Nb ₂ O ₅ per cc. of solution.	Nb ₂ O ₅ per cc. N/10.
1.	0.2224	7½	28.97	0.007677	0.00731
2.	0.2016	8½	26.20	0.007702	0.00783
3.	0.2338	7½	29.99	0.007795	0.00792
4.	0.2174	8½	27.21	0.007699	0.00782
5.	0.2174	10	23.22	0.007704	0.00783

TABLE II.

6.	0.2002	8	22.80	0.008781	0.008558
7.	0.2009	9	24.65	0.008150	0.007943
8.	0.2077	9	23.05	0.008291	0.008031
9.	0.2047	8	24.20	0.008121	0.007915
10.	0.2046	7	24.40	0.008385	0.008173
11.	0.2034	6	24.15	0.008422	0.008209
12.	0.2079	10½	24.10	0.008626	0.008408
13.	0.2115	8	24.15	0.008758	0.008536
14.	0.2086	9	23.75	0.008792	0.008569
15.	0.2054	9	23.10	0.008688	0.008469

TABLE III.

15.	0.2051	13	28.10	0.007300	0.007114
17.	0.1988	14	27.30	0.007281	0.007096
18.	0.2046	15	28.55	0.007166	0.006984
19.	0.2074	16	28.45	0.007290	0.007105
20.	0.2129	16	29.30	0.007266	0.007082
21.	0.2018	16	27.25	0.007405	0.007218
22.	0.2121	17	28.90	0.007337	0.007152

TABLE IV.—Different Samples of Oxide.

No.	Sample.	Nb ₂ O ₅ taken.	Time, mins.	KMnO ₄ , cc.	Nb ₂ O ₅ per cc. of sol.	Nb ₂ O ₅ per cc. N/10.
23.	I ₁	0.2148	10	28.00	0.007671	0.007477
24.	I ₁	0.2051	16	26.60	0.007711	0.007515
25.	I ₂	0.2017	27	26.80	0.007526	0.007335
26.	I ₂	0.2012	31	27.50	0.007316	0.007131
27.	I ₂	0.2010	24	26.70	0.007528	0.007337
28.	I ₂	0.2033	37	26.90	0.007557	0.007366
29.	I ₃	0.2079	23	27.60	0.007532	0.007341
30.	I ₃	0.2031	35	27.05	0.007508	0.007318
31.	II ₁	0.2011	20	27.85	0.007221	0.007038
32.	II ₁	0.2012	28	27.95	0.007199	0.007016
33.	II ₂	0.1997	16	27.80	0.007183	0.007002
34.	II ₂	0.2048	16	28.00	0.007314	0.007129
35.	II ₂	0.2035	16	27.75	0.007333	0.007148
36.	II ₃	0.2012	16	27.50	0.007316	0.007131
37.	II ₃	0.2031	18	27.80	0.007306	0.007121
38.	II ₃	0.2077	12	28.45	0.007301	0.007116
39.	II ₃	0.2033	15	27.85	0.007300	0.007115

TABLE V.

40.	IA	0.2015	6	27.90	0.007221	0.007038
41.	IA	0.2017	7	27.85	0.007242	0.007059
42.	II _{3a}	0.2055	13	27.70	0.007419	0.007231
43.	II _{3a}	0.2090	15	27.80	0.007518	0.007327
44.	II _{3b}	0.2223	16	30.55	0.007277	0.007092
45.	II _{3b}	0.2431	17	33.60	0.007235	0.007052

TABLE VI.

No.	Nb ₂ O ₅ taken.	Ta ₂ O ₅ taken.	Time, minutes.	KMnO ₄ , cc.	Nb ₂ O ₅ found.
46.	0.2051	0.050	15	27.15	0.1972
47.	0.2193	0.050	8	29.90	0.2171
48.	0.2039	0.050	6	27.40	0.1990
49.	0.2024	0.100	9	27.50	0.2001
50.	0.2005	0.100	8	27.50	0.1997
51.	0.1175	0.100	12	15.80	0.1148
52.	0.1098	0.100	9	15.60	0.1133
53.	0.1116	0.100	5	15.10	0.1097
54.	0.1394	0.200	10	19.30	0.1401
55.	0.1288	0.200	6	17.00	0.1235
56.	0.0513	0.200	7	6.85	0.0498

Procedure.—Inasmuch as every determination from this point was made in exactly the same manner, the exact details of the procedure are here given.

The oxide (or mixture of oxides) is fused with 5 grms. of potassium bisulphate in a 30 or 40 gm. platinum crucible. To the cooled mass 10 cc. of concentrated sulphuric acid is added, and heat carefully applied until a perfectly clear solution is obtained, which is allowed to cool, and the contents of the crucible transferred to a beaker, the crucible being rinsed with 30 cc. of concentrated sulphuric acid. The solution should be perfectly clear at this point (any cloudiness shows incomplete fusion). Two grms. of succinic acid are then added, and the contents of the beaker stirred for a short time, about 20 cc. of a saturated aqueous solution of succinic acid is then added in a fine stream from a wash-bottle with constant agitation, then water is added to a volume of 200 cc., and the solution heated to a temperature of 75° C. Meanwhile, the reductor is prepared by passing through it 200 cc. of 5 per cent sulphuric acid heated to 75° C., rejecting this acid, and filling again with 20 per cent sulphuric acid heated to 75° C. The niobium solution is then passed through the reductor, followed by 50 cc. of 20 per cent sulphuric acid, and then by 200 cc. of 5 per cent sulphuric acid. The reduced solution, which is dark brown in colour, is titrated with a standard potassium permanganate solution, the whole operation being carried out in an atmosphere of carbon dioxide. During the titration the solution first changes from brown to green, then through various shades of blue to colourless, the end-point being the characteristic colour of the potassium permanganate. The end-point is very sharp. After each determination a few centimetres of the zinc is removed from the top of the reductor and replaced by fresh material, this being necessary, as otherwise a layer of finely divided zinc accumulates which would ultimately clog the reductor (Table IV.).

These results indicate highest purity for Samples II₁ and II₂, while II₃ seems to show the presence of a slight amount of tantalum. All of samples "I" show the presence of a small amount of tantalum.

Purification of Oxides.—The above samples which indicate the presence of impurity were again purified as follows.—All of samples "I" were combined, fused with potassium bisulphate, &c., as usual in the fractional crystallisation of the double potassium fluorides. The solution of the double potassium fluorides was evaporated nearly to dryness, dissolved in the least amount of boiling water, and allowed to crystallise, yielding a crop of crystals which, upon careful examination showed the presence of some needles of K₂TaF₇. The mother-liquor from these crystals was decanted through a filter, and the crystals rejected. This mother-liquor was evaporated to fumes with sulphuric acid, boiled with water, &c., as usual, obtaining finally the oxide, designated IA.

Sample II₃ was purified in exactly the same manner as the combined samples "I" above, converting, however, both crystals and mother-liquor into oxide. That from the crystals being designated II_{3a}, and that from the mother-liquor II_{3b}.

Determinations were made on these samples with results as shown in Table V.

As was expected, Sample IA showed the effect of purification, giving results which agree, within the experimental error, with those of Samples II₁ and II₂. Similarly, Sample II_{3a} indicates the presence of tantalum in the product, whereas Sample II_{3b} showed the same degree of purity as Samples II₁, II₂, and IA.

Degree of Reduction of the Niobium.—The N/10 factor of the potassium permanganate solution was 1.0260.

1 cc. of this solution = 0.007232 Nb₂O₅ (a).

1 cc. of N/10 solution = 0.007052 Nb₂O₅ (a).

(a) This result is the average of the values obtained for Samples IA, II_{3b}, II₁, and II₂.

Molecular weight Nb₂O₅ = 267.

Hydrogen equivalent of Nb_2O_5 when reduced under the specified conditions $\frac{0.0267}{0.007052} = 3.786$.

Mols. of oxygen required to oxidise the product resulting from the reduction of one mol. of Nb_2O_5 under the specified conditions—

$$= \frac{3.786}{2} = 1.893.$$

$$5 - 1.893 = 3.107.$$

Therefore Nb_2O_5 is reduced to $\text{Nb}_2\text{O}_{3.107}$, corresponding nearly to the oxide $\text{Nb}_{20}\text{O}_{31}$.

Reduction by adding Unamalgamated Zinc to the Solution.—It was thought that there might be some advantage in reducing the niobium solution in a flask with zinc instead of by means of the Jones reductor. A blank determination was therefore made on the zinc as follows:—Eight grms. of C.P. 20-mesh zinc was added to a flask containing 40 cc. of concentrated sulphuric acid and 160 cc. of water, heated to 70° or 80°C ., and an atmosphere of carbon dioxide maintained. When the zinc was completely dissolved the solution was titrated in an atmosphere of carbon dioxide. Required, 0.2 cc. KMnO_4 .

A similar experiment using a solution containing 0.2000 gm. of Nb_2O_5 required 3.3 cc. of KMnO_4 , while it should have required nearly 30 cc. if the reduction had been complete.

Another experiment, using 10 grms. of zinc and 0.2051 Nb_2O_5 , heated to 90°C ., required 8 cc. KMnO_4 .

Another experiment using 5 grms. of 80-mesh zinc, and maintaining an atmosphere of hydrogen, required 1 cc. of KMnO_4 solution for 0.1490 gm. of Nb_2O_5 taken.

It is our opinion that the failure of these experiments in the reduction of the niobium was due to the fact that with the quite strong acid necessary in the solution the action on the zinc was so very rapid that the process could not continue for a sufficient time to effect any considerable reduction of the niobium without adding an excessive quantity of zinc.

Mixtures of Niobium and Tantalum.—Mixtures of Nb_2O_5 and Ta_2O_5 were next analysed as indicated below.

The Ta_2O_5 employed in these mixtures was passed through the reductor as a blank experiment, and the potassium permanganate solution used in the titration (0.2 cc.) deducted (Table VI.).

(To be continued).

A REVISION OF THE ATOMIC WEIGHTS OF IODINE AND SILVER.*

(PRELIMINARY PAPER).

By GREGORY PAUL BAXTER and GEO. STEPHEN TILLEY.

The Analysis of Iodine Pentoxide.

For some time it has been apparent that Stas's researches upon the atomic weight of silver, upon which the value now in use depends, are somewhat at fault. The need for a re-determination of the ratio of this constant to the atomic weight of oxygen is especially pressing, since silver has been very frequently used as the basis for exact work upon atomic weights, both directly and also indirectly, through its relation to the atomic weights of the halogens in the analysis of metallic halides.

The problem is made difficult, however, by the fact that the only known definite compounds of silver with oxygen are difficult if not impossible to prepare in a pure state, besides containing so small a percentage of oxygen that the experimental error would be greatly magnified in the calculation. All other methods involve the knowledge of the exact ratio of at least one other atomic weight to that of silver or oxygen, the accuracy of the process diminishing

with the number of atoms involved. Among the various classes of compounds the analysis of which may afford the desired information, oxides are of especial interest because the knowledge of the ratio of only one atomic weight to that of silver is involved. The difficulty and uncertainty in analysing metallic oxides make them unsuited for the purpose (Richards and Baxter, *Proc. Am. Acad.*, 1899, xxxv., 61; 1900, xxxv., 253). The ratios of the atomic weights of silver and the halogens are known with greater exactness than in the case of most elements, hence to determine the ratio of any one of the halogens to that of oxygen will serve the purpose equally well. The only compound of a halogen and oxygen of considerable stability is iodine pentoxide. This substance is, however, quite stable through a fairly wide range of conditions, and its analysis offered enticing possibilities. To be sure, the percentage of oxygen in the compound is not high, but this disadvantage is, in part, counterbalanced by the fact that the ratio of the atomic weight of iodine to that of silver is greater than in the case of most elements.

The Preparation of Iodic Acid.—Iodine pentoxide may be readily prepared by dehydration of iodic acid at a comparatively low temperature. Of the various methods for preparing the latter substance, by far the most satisfactory for the present purpose is the oxidation of iodine with fuming nitric acid. The volatile by-products of the reaction, oxides of nitrogen and water, as well as the excess of nitric acid, may be removed by heating, and the acid may be crystallised from aqueous solution.

Iodine was purified for most of the preparations by the methods already described by one of us (Baxter, *Proc. Am. Acad.*, 1904, xl., 421). These consisted usually in a preliminary distillation of commercial iodine from solution in commercial aqueous potassium iodide. The iodine was then twice reduced to hydriodic acid by hydrogen sulphide and water, and the hydriodic acid was subsequently oxidised by re-crystallised permanganate, with intermediate boiling of the hydriodic acid solution to eliminate cyanogen as hydrocyanic acid (Richards and Singer, *Am. Chem. Journ.*, 1902, xxvii., 205). In this way, since only five-eighths of the iodine is set free from hydriodic acid by permanganate, the iodine was three times distilled from a solution of an iodide, the iodide being of greater purity in each succeeding distillation. It has already been shown that three such distillations are sufficient to remove completely chlorine and bromine (Baxter, *loc. cit.*; also *Proc. Am. Acad.*, 1905, xli., 73), so that there can be no question of the freedom of the resulting iodine from those closely related elements. The final product was once distilled with water into a Jena glass flask cooled with running water, and the resulting solid was washed with the purest water upon a porcelain Gooch crucible containing no mat.

Pure fuming nitric acid was prepared by distilling the best commercial product several times, with rejection of the first and last thirds, until the distillate, after dilution, gave no test for chloride with silver nitrate in a nephelometer (Richards and Wells, *Am. Chem. Journ.*, 1904, xxxi., 235; 1906, xxxv., 510). A quartz condensing tube was used in these distillations, and the final product was collected in a quartz vessel. In this way the introduction of silica and alkalis from glass vessels was avoided. Fused quartz vessels have already been shown to be essentially insoluble in acid solutions (Mylius and Meusser, *Zeit. Anorg. Chem.*, 1905, xlv., 221; Baxter and Hines, *Journ. Am. Chem. Soc.*, 1906, xxviii., 1565).

The reaction between iodine and fuming nitric acid proceeds slowly at ordinary temperatures, with the formation of oxides of nitrogen and nitro-iodic acid. Heat hastens the reaction, and also breaks up the nitro-iodic acid into nitric oxide, iodine, and iodic acid. If the nitric acid is in large excess the iodine is converted into iodic acid without loss, and the iodic acid remains insoluble in the residual concentrated nitric acid. If the iodine is in excess, the reaction proceeds until the nitric acid is so dilute, owing to the production of water in the reaction, as to be without further effect upon the iodine, although the acid

* Contribution from the Chemical Laboratory of Harvard College. From the *Journal of the American Chemical Society*, xxxi., No. 2.

is still so concentrated that the iodic acid remains essentially insoluble. Nitric acid of this concentration dissolves considerable quantities of iodine, however.

Since the largest quartz vessel at first available was a 100 cc. transparent fused quartz flask, the most convenient method for making the iodic acid was found to be to treat a large quantity of iodine in the flask with successive portions of fuming nitric acid. After the introduction of the iodine, nitric acid was distilled directly into the flask through the quartz condenser. The flask was then warmed until the nitric acid was spent. The spent acid was removed as completely as possible by drainage, and was replaced by fresh acid, and the process was repeated until the iodine appeared to be completely oxidised. Dissolved iodine was recovered from the spent acid by dilution. After the removal of the last portion of the acid, the iodic acid was dissolved in the smallest possible amount of the purest water, and the solution was evaporated to dryness in a dish of fused quartz in order to expel nitric acid and unchanged iodine, for the removal of nitric acid by crystallisation is very slow. During this evaporation the dish was placed upon a large watch-glass on a sand-bath, and was surrounded by a large bottomless beaker. The dish was further protected by being covered with a bottomless flask, through the neck of which a current of pure dry air was introduced in order to hasten evaporation. The air was freed from organic matter by passing over hot copper oxide in a hard glass tube, and was purified and dried by means of a solution of potassium hydroxide and solid caustic potash. The purifying apparatus was constructed wholly of glass.

The residue from the evaporation was dissolved in the purest water, and evaporated in a quartz dish with the same precautions as above until a film of solid appeared on the surface of the liquid. This solid is not iodic acid, but is probably a compound having less water, since it was necessary to induce the crystallisation of the acid itself by inoculation. If left to itself the acid crystallises very slowly, some days being necessary for the establishment of equilibrium. It is economical, however, to wait for the establishment of equilibrium, since the solubility of the acid at room temperature is so high, a saturated solution at 20° containing over 75 per cent of acid. The first crop of crystals was drained as completely as possible, usually with centrifugal drainage in a platinum centrifugal machine, and the product was twice re-crystallised (Baxter, *Journ. Am. Chem. Soc.*, 1908, xxx., 286). On account of the high solubility of the acid and the low temperature coefficient of solubility between 0° and 100° the yields of acid were very small, hence the mother-liquors were worked up for several successive yields of crystals. The thrice re-crystallised acid was preserved in a desiccator containing solid caustic potash. It was designated Sample 1.

The solutions of iodic acid, as well as the solid substance, and even iodine pentoxide made from the acid, possessed to a slight degree a peculiar odour which may be described as "aromatic." This odour persisted through the crystallisation although with continual diminution, but was not entirely absent from acid which had been crystallised three times. It was later proved that the odour is not due to the acid itself, because after a sufficient number of crystallisations the odour disappears. Furthermore, it was experimentally proved that no appreciable amount of iodine was contained in this vapour, for when a concentrated solution of the acid is boiled no iodine can be detected in the distillate, and when a current of air is conducted over the solid at ordinary temperatures into a solution of sulphur dioxide no iodine can be found in the sulphurous acid solution. Even at high temperatures the pentoxide loses in weight very slowly, 10 grms. losing only 1 mgrm. at 240° in four hours. By far the greater part of this loss is due to decomposition of the pentoxide, for free iodine can be easily detected in the air which has passed over the substance.

The possibility of the presence of metallic impurity in the iodic acid, arising from the action of iodine on the glass

of the flask in which it was condensed, was tested by evaporating to dryness the mother-liquor of the last crystallisation of the original solution, and heating the residue in a weighed platinum boat in a current of pure dry air until the pentoxide was completely decomposed. The boat gained in weight only 0.0006 gm., part of this gain being due to the formation of platinum iodide. Faint tests for sodium and calcium only could be obtained with the residue in the spectroscopic.

The Preparation of Pure Silver.—Silver was purified by methods already found in this laboratory to be effective for the purpose. A dilute solution of silver nitrate was first precipitated with hydrochloric acid in excess, and the precipitate was thoroughly washed with pure water. The chloride was next reduced by means of invert sugar and an excess of sodium hydroxide, and the metal after long continued washing by decantation, was fused upon charcoal. After the buttons had been cleansed by scrubbing with sand and etching with nitric acid, they were dissolved in nitric acid, and the silver was precipitated as metal by means of ammonium formate made from re-distilled ammonia and formic acid. This precipitate in turn was thoroughly washed, and the metal was fused in the flame of a carefully cleaned blast-lamp in a crucible of lime made from purified calcium nitrate and carbonate. After being cleansed as before, the buttons were electrolysed in a cell in which a pile of these buttons served as anode, the cathode being a bar of the purest silver and the electrolyte being a concentrated solution of silver nitrate made from one of the buttons. Next, the electrolytic crystals, after being washed and dried, were fused in a current of pure electrolytic hydrogen in an unglazed porcelain boat lined with the purest lime (see Note). The resulting buttons were cut into fragments of from 3 to 6 grms. with a fine jeweller's saw, etched with small portions of dilute nitric acid until the acid used in etching was free from iron, and finally the fragments were washed and thoroughly dried in a vacuum at about 400°. Two different specimens of silver were prepared in essentially the same way; Samples A and B.

(NOTE.—Fusion in hydrogen (Baxter, *Proc. Am. Acad.*, 1903, xxxix., 249) is probably safer than fusion in a vacuum, since it eliminates the possibility of the taking up of sulphur by the silver from the rubber ring used in fitting the hollow brass stoppers into the porcelain fusion tube. Richards and Wells—*Pub. Car. Inst.*, 1905, No. 28—have shown that silver fused in hydrogen is certainly as pure as any other).

The Conversion of Iodic Acid into Iodine Pentoxide.—The conversion of the iodic acid into iodine pentoxide was effected by heating the substance in a current of dry gas. At the beginning of the research the hope was entertained that the final product might be sublimed. In no experiment, however, have we been able to detect the least trace of sublimation, even when the pentoxide was heated to the decomposition point. Iodic acid may be made to lose all its water of composition without fusion, and consequently it was to be expected that under these conditions dehydration could be made nearly, if not quite, complete. T. W. Richards has already pointed out that a solid which loses water of composition without fusion is left in the form of a skeleton, from the innermost interstices of which the water vapour may escape, while, if fusion takes place during drying, a portion of the original salt may be enclosed with an impervious coating of anhydrous salt so that escape of water is impossible (*Zeit. Phys. Chem.*, 1903, xlvii., 194).

It is commonly stated that the dehydration of iodic acid takes place in two stages, two-thirds the water being lost below 130° and the remainder at about 200°. (For a discussion of this subject see Groschuff, *Zeit. Anorg. Chem.*, 1905, xlvii., 333). The acid itself, if heated rapidly, melts at 110° with the separation of the solid phase $I_2O_5 \cdot HIO_3$, although this second phase shows no indication of melting up to the temperature of the second stage in the dehydration. Our earlier experience was not in accordance with the above statements. The acid, when heated to about 110° lost all its water of composition at this temperature,

This was shown conclusively in one experiment by heating a weighed amount of iodic acid for some time at about 110° , and then re-weighing. The acid lost the amount of water theoretically necessary for the formation of the pentoxide, and further heating to 300° produced only a negligible diminution in weight. On one later occasion, however, when a comparatively crude specimen of acid was being dehydrated, the second phase unexpectedly appeared, and in all subsequent experiments the same result was obtained, no matter what the source of the iodic acid or how carefully the apparatus was cleaned before use. This point is additional proof that the second phase is a definite chemical compound. The obvious explanation of the phenomenon is that the laboratory became inoculated with "germs" of the second phase, so that its formation was thereafter always induced.

The iodic acid was dehydrated in a platinum boat contained in a hard glass tube heated by a solid aluminium oven. This oven, for the suggestion of which we are indebted to Dr. Arthur Stähler, of the University of Berlin, consisted of two machined aluminium blocks, $15 \times 13 \times 5$ cm., the upper surface of one block and the lower surface of the other being grooved to contain the hard glass tube, when one block was placed upon the other. The blocks were further bored to contain a thermometer in such a way that the bulb was located within half a centimetre of the middle of the hard glass tube. When heated with a small Bunsen flame, this bath could be regulated in temperature to within 1° or 2° without the least difficulty, even without the jacket of asbestos paper which was usually employed. Thermometers placed inside the hard glass tube and in the cavity in the blocks registered the same temperature within a degree even when the oven was heated to 300° .

At first, the air was purified and dried by passing over hot copper oxide in a hard glass tube, then through two towers containing beads moistened with silver nitrate and caustic potash solutions, respectively, and finally through four towers containing beads moistened with concentrated sulphuric acid to which a small quantity of potassium dichromate had been added in order to prevent any possibility of reduction. The apparatus was constructed wholly of glass with ground or fused joints, rubber and grease being carefully avoided. When heated in a current of air thus purified and dried, even the purest iodine pentoxide became somewhat brown owing possibly to liberation of iodine. The use of electrolytic oxygen in place of air failed to prevent this phenomenon. Finally, it was found that if the air was dried more thoroughly, by means of re-sublimed phosphorus pentoxide, the difficulty could be avoided. The cause of this marked catalytic effect from the minute quantity of moisture which is not absorbed by sulphuric acid was not determined.

The hard glass tube in which the heating was conducted formed part of a bottling apparatus by means of which the boat could be transferred to a weighing bottle, without an instant's exposure to moist air. Similar apparatus was first used for the purpose by Richards (*Proc. Am. Acad.*, 1894, xxx., 383), and was modified and improved by Richards and Parker (*Ibid.*, 1896, xxii., 59). Although these precautions were taken to prevent exposure of the substance to moisture before weighing, little danger was to be feared from this source, for in air ordinarily moist the pentoxide absorbs water very slowly. For instance, 4.4 grms. of pentoxide, when exposed in the platinum boat to the air of the laboratory for two hours, gained only 0.0008 grm.

Even when dried under the most favourable conditions the above mentioned darkening of the pentoxide took place if the temperature rose much over 250° . Accordingly, the temperature was not allowed to pass this point in drying the substance for analysis. Furthermore, since it was by no means certain that every trace of water could be expelled from the pentoxide at this temperature, and since it seemed probable that the amount of water retained would vary with the temperature and time of treatment, the conditions in the different experiments were made as nearly as possible identical.

The details of manipulation were as follows:—The crystals of iodic acid were powdered in a new smooth agate mortar together with a small quantity, about 2 per cent, of the weight of the acid, of the phase produced in the first stage in the dehydration. This step was of advantage in catalysing the first stage in the dehydration, for frequently, when the precaution of thus inoculating the iodic acid was omitted, the temperature reached 130° before dehydration began, whereas when this precaution is taken the water first appears as low as 85° . Since the iodic acid itself melts at 110° when in contact with the phase produced at this temperature, it seemed better to prevent the acid from reaching this temperature until the first stage in the dehydration was past. As a matter of fact, preliminary water determinations in the dried material indicated a slightly larger proportion of water in acid which had not been inoculated with the second phase.

The weighed boat, containing from 6 to 10 grms. of the iodic acid, was next heated in a slow current of air at 90° to 110° until the first two-thirds of the water of composition had been given off by the iodic acid and had been expelled from the tube by the current of dry air. The temperature was then raised until the second portion of water was given off. Usually the pentoxide began to form at about 220° . There is no evidence of fusion at this point, even if the temperature rises much above 200° before all the remaining water is expelled. After all the water had disappeared the temperature was raised to 240° , and maintained at this point for four hours. Then the boat was transferred to the weighing bottle, allowed to stand in the desiccator with the counterpoise for some time, and was weighed.

(To be continued).

SOME FORMS OF FOOD ADULTERATION AND SIMPLE METHODS FOR THEIR DETECTION.*

By W. D. BIGELOW, Chief of the Division of Foods,
and
BURTON J. HOWARD, Chief of the Microchemical Laboratory.

(Continued from p. 249).

EXAMINATION OF CERTAIN CLASSES OF FOODS.

Canned Vegetables.

As before stated, canned vegetables are relatively free from adulteration by means of foreign substances. The different grades of products may with care be readily detected by the general appearance of the sample. The purchaser is, of course, at the disadvantage of not being able to see the product until the can is opened. By a study of the different brands available in the vicinity, however, he can readily select those which are preferable. As stated in an earlier part of the *Bulletin*, canned tomatoes sometimes contain an artificial colouring matter, which may be detected as already described.

Canned sweet corn is sometimes sweetened with saccharin, which may be detected as already described.

It is believed that, as a rule, canned vegetables are free from preservatives, although some instances of chemical preservation have recently been reported in North Dakota, and some imported tomatoes have been found by this Bureau to be artificially preserved. The presence of copper, often used for the artificial greening of imported canned peas, beans, spinach, &c., may be detected as already described.

Coffee.

There are a number of simple tests for the presence of the adulterants of ground coffee. These tests are called simple because they can be performed without the facilities of the chemical laboratory, and by one who has not had the experience and training of a chemist. It must be

* *Bulletin* No. 100, Bureau of Chemistry, U.S. Department of Agriculture.

understood, however, that they require careful observation and study, and that one must perform them repeatedly in order to obtain reliable results. Before applying them to the examination of an unknown sample, samples of known character should be secured and studied. Unground coffee may be ground in the home and mixed with various kinds of adulterants, which can also be secured separately. Thus the articles themselves in known mixtures may be studied, and when the same results are obtained with unknown samples they can be correctly interpreted. These tests are well known in the laboratory, and may be used in the home of the careful housewife who has the time and perseverance to master them.

Physical Tests.—The difference between the genuine ground coffee and the adulterated article can often be detected by simple inspection with the naked eye. This is particularly true if the product be coarsely crushed rather than finely ground. In such condition pure coffee has a quite uniform appearance, whereas the mixtures of peas, beans, cereals, chicory, &c., often disclose their heterogeneous nature to the careful observer. This is particularly true if a magnifying glass be employed. The different articles composing the mixture may then be separated by the point of a penknife. The dark gummy-looking chicory particles stand out in strong contrast to the other substances used, and their nature can be determined by one who is familiar with them by their astringent taste.

The appearance of the coffee particles is also quite distinct from that of many of the coffee substitutes employed. The coffee has a dull surface, whereas some of its substitutes, especially leguminous products, often present the appearance of having a polished surface.

After a careful inspection of the sample with the naked eye, or, better, with a magnifying glass, a portion of it may be placed in a small bottle half full of water and shaken. The bottle is then placed on the table for a moment. Pure coffee contains a large amount of oil, by reason of which the greater portion of the sample will float. All coffee substitutes and some particles of coffee sink to the bottom of the liquid. A fair idea of the purity of the sample can often be determined by the proportion of the sample which floats or sinks.

Chicory contains a substance which dissolves in water, imparting a brownish red colour. When the suspected sample therefore is dropped into a glass of water, the grains of chicory which it contains may be seen slowly sinking to the bottom, leaving a train of a dark brown coloured liquid behind them. This test appears to lead to more errors in the hands of inexperienced operators than any other test here given. Wrong conclusions may be avoided by working first with known samples of coffee and chicory as suggested above.

Many coffee substitutes are now sold as such and are advertised as more wholesome than coffee. Notwithstanding the claims that are made for them, a few of them contain a considerable percentage of coffee. This may be determined by shaking a teaspoonful in a bottle half full of water, as described above. The bottle must be thoroughly shaken so as to wet every particle of the sample. Very few particles of coffee substitutes will float.

Chemical Tests.—Coffee contains no starch, while all of the substances, except chicory, used for its adulteration and in the preparation of coffee substitutes contain a considerable amount of starch. The presence of such substitutes may therefore be detected by applying the test for starch as given later on. In making this test less than a quarter of a teaspoonful of ground coffee should be used, or a portion of the ordinary infusion prepared for the table may be employed after dilution. The amount of water that should be added can only be determined by experience.

Condimental Sauces.

Tomato catsup and other condimental sauces are frequently preserved and coloured artificially. The preservatives employed are usually salicylic acid and benzoic

acid or their sodium salts. These products may be detected by the methods already described.

Coal-tar colours are frequently employed with this class of goods, especially with those of a reddish tint, like tomato catsup. They may be detected by the methods already described.

Butter.

Methods are available which, with a little practice, may be employed to distinguish between fresh butter, renovated or process butter, and oleomargarine.

These methods are commonly used in food and dairy laboratories, and were originally suggested as household tests (Patrick, "Household Tests for the Detection of Oleomargarine and Renovated Butter," *Farmer's Bulletin*, No. 131). They give reliable results. At the same time considerable practice is necessary before we can interpret correctly the results obtained. Some process butters are on the market which can be distinguished from fresh butter only with extreme difficulty. During the last few years considerable progress has been made in the attempt to renovate butter in such a way that it will appear like fresh butter in all respects. A study must be made of these methods if we would obtain reliable results.

The "spoon" test has been suggested as a household test, and is commonly used by analytical chemists for distinguishing fresh butter from renovated butter and oleomargarine. A lump of butter two or three times the size of a pea is placed in a large spoon, and heated over an alcohol or Bunsen burner. If more convenient, the spoon may be held above the chimney of an ordinary kerosene lamp, or it may even be held over an ordinary illuminating gas burner. If the sample in question be fresh butter it will boil quietly, with the evolution of many small bubbles throughout the mass which produce a large amount of foam. Oleomargarine and process butter, on the other hand, sputter and crackle, making a noise similar to that heard when a green stick is placed in a fire. Another point of distinction is noted if a small portion of the sample be placed in a small bottle and set in a vessel of water sufficiently warm to melt the butter. The sample is kept melted from half-an-hour to an hour, when it is examined. If renovated butter or oleomargarine, the fat will be turbid, while if genuine fresh butter the fat will almost certainly be entirely clear.

To manipulate what is known as the "Waterhouse" or "milk" test, about 2 ounces of sweet milk are placed in a wide-mouthed bottle, which is set in a vessel of boiling water. When the milk is thoroughly heated a teaspoonful of butter is added, and the mixture stirred with a splinter of wood until the fat is melted. The bottle is then placed in a dish of ice water and the stirring continued until the fat solidifies. Now, if the sample be butter, either fresh or renovated, it will be solidified in a granular condition, and distributed through the milk in small particles. If, on the other hand, the sample consist of oleomargarine it solidifies practically in one piece, and may be lifted by the stirrer from the milk.

By these two tests, the first of which distinguishes fresh butter from process or renovated butter and oleomargarine, and the second of which distinguishes oleomargarine from either fresh butter or renovated butter, the nature of the sample under examination may be determined.

Milk.

The oldest and simplest method of adulterating milk is by dilution with water. This destroys the natural yellowish white colour and produces a bluish tint, which is sometimes corrected by the addition of a small amount of colouring matter.

Another form of adulteration is the removal of the cream and the sale as whole milk of skimmed or partially skimmed milk. Again, the difficulty experienced in the preservation of milk in warm weather has led to the widespread use of chemical preservatives.

Detection of Water.—If a lactometer or hydrometer, which can be obtained of dealers in chemical apparatus,

be available, the specific gravity of milk will afford some clue as to whether the sample has been adulterated by dilution with water. Whole milk has a specific gravity between 1.027 and 1.033. The specific gravity of skimmed milk is higher, and milk very rich in cream is sometimes lower than these figures. It is understood, of course, that by specific gravity is meant the weight of a substance with reference to the weight of an equal volume of water. The specific gravity of water therefore is exactly 1. It is obvious that if water be added to a milk with the specific gravity of 1.030, the specific gravity of the mixture will be somewhat below those figures.

An indication by means of a hydrometer or lactometer below the figure 1.027 therefore indicates either that the sample in question is a very rich milk, or that it is a milk (perhaps normal, perhaps skimmed) that has been watered. The difference in appearance and nature of these two extremes is sufficiently obvious to make use of the lactometer or hydrometer of value as a preliminary test of the purity of milk.

Detection of Colour.—As previously stated, when milk is diluted by means of water the natural yellowish white colour is changed to a bluish tint, which is sometimes corrected by the addition of colouring matter. Coal-tar colours are usually employed for this purpose. A reaction for these colours is often obtained in the method given below for the detection of formaldehyde. When strong hydrochloric acid is added to the milk in approximately equal proportions before the mixture is heated a pink tinge sometimes is evident if a coal-tar colour has been added.

Detection of Formaldehyde.—Formaldehyde is the substance most commonly used for preserving milk, and is rarely, if ever, added to any other food. Its use is inexcusable, and especially objectionable in milk served to infants and invalids.

To detect formaldehyde in milk three or four tablespoonfuls of the sample are placed in a teacup with at least an equal amount of strong hydrochloric acid and a piece of ferric alum about as large as a pinhead, the liquids being mixed by a gentle rotary motion. The cup is then placed in a vessel of boiling water, no further heat being applied, and left for five minutes. At the end of this time, if formaldehyde be present, the mixture will be distinctly purple. If too much heat is applied, a muddy appearance is imparted to the contents of the cup.

Caution.—Great care must be exercised in working with hydrochloric acid, as it is strongly corrosive. It must not come in contact with the flesh or clothes of the operator nor with any metallic vessels, and must be greatly diluted with water before it is poured into the sink.

(To be continued).

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, November 11th, 1909.

Sir ARCHIBALD GEIKIE, K.C.B., President in the Chair.

PAPERS were read as follows, the summaries here printed having been supplied by the authors:—

“*Vacuolation of the Blood-platelets: an Experimental Proof of their Cellular Nature.*” By H. C. ROSS.

“*Further Results of the Experimental Treatment of Trypanosomiasis, being a Progress Report to a Committee of the Royal Society.*” By H. G. PLIMMER and Captain W. B. FRY, R.A.M.C.

“*Hillhusia mirabilis, a Giant Sulphur Bacterium.*” By G. S. WEST and B. M. GRIFFITHS.

“*Modes of Division of Spirochaeta recurrentis and S. duttoni as Observed in the Living Organisms.*” By H. B. FANTHAM, D.Sc. (Lond.), and Miss ANNIE PORTER, B.Sc. (Lond.).

“*Supposed presence of Carbon Monoxide in Normal Blood, and in the Blood of Animals Anaesthetised with Chloroform.*” By G. A. BUCKMASTER and J. A. GARDNER.

In a paper published in 1898, Desgrez and Nicloux stated that the normal blood of Paris dogs contains about 1.6 cc. of carbon monoxide per litre, and that when the animals are anaesthetised by chloroform the amount increases to 2.5 to 6 cc., according to the duration of anaesthesia. Their method of estimating carbon monoxide consisted in passing the blood gases over iodine pentoxide at 150° C., and determining the iodine liberated by the method of Rabourdin. We have carefully re-investigated the question, making use of Haldane's method of estimating carbon monoxide by means of diluted blood, after having previously ascertained that far smaller quantities of this gas than those found by the French observers in normal blood gases could be readily detected. We find that *neither normal cats' blood nor the blood of cats anaesthetised by chloroform contains any detectable trace of carbon monoxide.* We also found that most of the chloroform in the blood comes off with the gases when extracted at 40° C. In order to arrive at an explanation of Nicloux's results we (1) repeated his experiments with variations, investigated (2) the effect of heat on iodine pentoxide, (3) the effect of chloroform vapour on iodine pentoxide, and (4) the effect of chloroform vapour on alkalis. The latter experiments show that chloroform vapour is readily decomposed by passing over solid potash, and also by the reagents used in gas analysis, with the production of carbon monoxide.

We conclude from our experiments (1) that chloroform is not decomposed in the blood with formation of carbon monoxide, (2) the iodine liberated in the experiments of Nicloux was due to some extent to the direct decomposition of the iodine pentoxide by the chloroform vapour in his blood gases, but mainly to the carbon monoxide produced by the action of this chloroform on the solid potash over which he passed the blood gases in order to free them from carbon dioxide.

“*Origin and Destiny of Cholesterol in the Animal Organisms.* Part VI. *The Excretion of Cholesterol by the Cat.*” By G. W. ELLIS and J. A. GARDNER.

In this paper the results of a number of estimations of the cholesterol content of the faeces of cats fed on a variety of diets—animal and vegetable—of known cholesterol content, are described.

It was found that cats behave similarly to dogs when fed on meat diets, but the tendency for the change of cholesterol into coprosterol appears to be greater in the case of cats. The change is, however, never complete unless the diet contains a considerable amount of fat. In all these experiments the total cholesterol and coprosterol excreted was considerably less than that taken in with the food. Without considering the cholesterol poured into the gut with the bile, the percentage deficit was 50 to 60, an average loss of about 0.08 gm. per day.

In the case of vegetable diets free from cholesterol or phytosterol, the weights of food necessary to keep the animals in condition were larger, and the amounts of faeces very much larger, than in the case of meat diets. Small amounts of cholesterol were excreted, averaging about 0.03 gm. per day, but no change into coprosterol took place. In the case of artificial diets to which measured quantities of cholesterol or phytosterol were added, no excess of cholesterol above that administered was recovered from the faeces. The bearing of these results on hypotheses advanced in former papers of the series is discussed.

“*Elasticity of Rubber Balloons and Hollow Viscera.*” By Prof. W. A. OSBORNE. (With a Note by W. SUTHERLAND).

CHEMICAL SOCIETY.

Ordinary Meeting, November 4th, 1909.

Professor HAROLD B. DIXON, F.R.S., President, in the Chair.

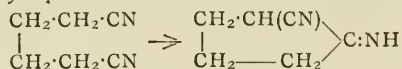
MESSRS. R. MÜLLER and H. S. WILLS were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Arthur Fordshaw, M.Sc., 104, Holly Road, Handsworth, Birmingham; Alexander David Gardiner, 6, Wellfield Terrace, Springburn, Glasgow; Eric John Holmyard, 7, Manor Street, Cambridge; Francis Hugh Ping, 10, Forest Place, Whipp's Cross Road, Leytonstone, N.E.; Richard Vernon Wheeler, D.Sc., British Coal Dust Experiments Committee, Altofts Colliery, Normanton.

Of the following papers, those marked * were read:—

*246. "The Formation and Reactions of Imino-compounds. Part XI. The Formation of 1-Imino-2-cyanocyclopentane from Adiponitrile." By JOSELYN FIELD THORPE.

A method was described by which $\alpha\delta$ -dicyanobutane (adiponitrile) can be completely converted into 1-imino-2-cyanocyclopentane in accordance with the scheme:—



DISCUSSION.

The PRESIDENT asked whether, if the second cyano-group was necessary for the reaction to proceed (though it remains at the end unchanged), it did not point to a transitory interaction between this group and the catalyst?

Dr. J. F. THORPE, in reply, said that the precise mechanism of the reaction was still open to question, but the nitrile group remaining unaffected apparently had some influence, since its presence seemed to be essential.

In reply to Dr. MORGAN, he stated that the use of piperidine, diethylamine, and other catalytic agents of that type did not lead to the formation of imino-compounds.

In reply to Mr. BALY, Dr. THORPE said that so far as he knew there was no chemical evidence of a hydrogen atom of the methylene group of ethyl cyanoacetate wandering to the nitrogen atom under the influence of sodium ethoxide.

*247. "Studies in the Camphane Series. Part XXVII. Camphorylphenyltriazen (Camphordiazoaminobenzene) and its Bearing on the Constitution of Diazoamino-compounds." By MARTIN ONSLOW FORSTER and CHARLES SAMUEL GARLAND.

From a study of the compounds derived from amino-camphor and from methylaminocamphor by coupling these bases with diazonium salts, the authors conclude that aliphatic-aromatic diazoamino-compounds must be represented by the expression $\text{X}\cdot\text{N}\cdot\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$, the hydrogen atom of the triazen nucleus taking up a position of superior stability in the neighbourhood of the phenyl group rather than that of the alkyl radicle, X.

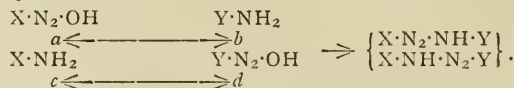
DISCUSSION.

Dr. MORGAN said that the authors' experiments amply justified the conclusions which they deduced in regard to the constitution of mixed aliphatic-aromatic diazoamines.

With reference to mixed diazoamines containing two aryl (benzenoid) groups X and Y, he could not, in the present state of knowledge, share Dr. Forster's belief that the coupled product of diazonium salt, $\text{X}\cdot\text{N}_2\text{Cl}$, and aromatic amine, $\text{Y}\cdot\text{NH}_2$, is entirely either $\text{X}\cdot\text{N}_2\cdot\text{NH}\cdot\text{Y}$ or $\text{X}\cdot\text{NH}\cdot\text{N}_2\cdot\text{Y}$. He preferred to regard the product, formed under the ordinary experimental conditions, as a mixture of these two isomeric diazoamines.

The observations of Griess, Meldola, Schraube, Hantzsch, and others showed conclusively that, when a diazonium salt and an aromatic amine are dissolved together in dilute acid, a certain amount of rearrangement occurs consequent

on the migration of diazo-nitrogen. The solution, if only feebly acid, then contains the following four reagents, a, b, c, and d (two diazo-hydroxides and two primary aromatic amines), produced by hydrolysis from their respective salts.



In the formation of the mixed diazoamine, coupling occurs along the lines ab and cd, with the result that the precipitated product is a mixture in which the proportions of $\text{X}\cdot\text{N}_2\cdot\text{NH}\cdot\text{Y}$ and $\text{X}\cdot\text{NH}\cdot\text{N}_2\cdot\text{Y}$ depend on the extent to which the migration of diazo-nitrogen has occurred.

The same result is obtained whether one starts with $\text{X}\cdot\text{N}_2\text{Cl}$ and $\text{Y}\cdot\text{NH}_2$ or with $\text{Y}\cdot\text{N}_2\text{Cl}$ and $\text{X}\cdot\text{NH}_2$. Migration of diazo-nitrogen occurs in either case; the same four reagents, a, b, c, and d, become effective, and their interaction determines the nature of the coupled product.

Dr. J. F. THORPE pointed out that if the system of three nitrogen atoms with a double valency between two of them described by Dr. Forster could be considered as analogous to the system of two carbon atoms and one oxygen atom ($\text{C}\cdot\text{C}\cdot\text{O}$), as in ethyl acetoacetate, or to the system of three carbon atoms with a double valency between two of them ($\text{C}\cdot\text{C}\cdot\text{C}$), as in glutamic acid, then any hydrogen attached to the extreme nitrogen atoms might be regarded for experimental purposes as being attached to the central nitrogen atom, thus:—



in the same manner as in glutamic acid.

In no case of this kind would there be reasonable hope of obtaining any trustworthy chemical evidence respecting the position of the hydrogen atom.

Dr. FORSTER was prepared to admit that aromatic diazoamino-compounds, when produced in the coupling process, exposed to light, and re-crystallised from hot solvents, behaved as Dr. Morgan indicated, namely, as a mixture of two isomeric diazoamines, but he attributed this to an alteration of $\text{X}\cdot\text{N}_2\cdot\text{NH}\cdot\text{Y}$ into $\text{X}\cdot\text{NH}\cdot\text{N}_2\cdot\text{Y}$, effected by the environment, such alteration proceeding with greater facility when the attraction exerted by Y for the hydrogen in the triazen chain did not differ greatly from that exerted by X. He was led to this conclusion principally by three circumstances.

1. The numerous cases of resolution by acids upon which current views regarding the constitution of aromatic diazoamino-compounds are based have been studied most frequently at temperatures ranging from that of the laboratory to 100°, instead of at zero or below.

2. When prepared by Dimroth's method, from aryl-azoimide and magnesium aryl halide, α -naphthylphenyltriazen is resolved by alcoholic hydrogen chloride below zero into α -naphthyl-diazonium chloride and aniline, unaccompanied by α -naphthylamine.

3. There does not appear to have been recorded a case in which two isomeric diazo-carbamides have arisen by direct action of phenylcarbimide on a diaryltriazen.

248. "Dynamics of the Reaction between Iodine and Acetone." By HARRY MEDFORTH DAWSON and MAY SYBIL LESLIE.

The physical properties of solutions of iodine in acetone are abnormal, and it has been found that this is due to a reaction resulting in the formation of hydrogen iodide and one or more iodoacetones. At the ordinary temperature the reaction takes place fairly rapidly, but is incomplete, indicating that the change is reversible.

In order to elucidate its mechanism, the authors have made measurements of the velocity of the reaction, the rate of change being diminished by dissolving the reacting substances in various inert solvents. In aqueous solution, the reaction proceeds much more nearly towards com-

pletion than it does in carbon tetrachloride, benzene, nitrobenzene, methyl alcohol, or methyl acetate. On the other hand, the velocity of the change in neutral solution appears to be much slower in water than it is in the other solvents used.

A detailed examination of the reaction in aqueous solution has shown that in presence of acids the rate of disappearance of the iodine is constant when the acetone is present in relatively large excess. In solutions acidified with sulphuric acid, the velocity is proportional to the concentration of the acid and also to that of the acetone. If no foreign acid is added, an autocatalytic effect is observed, due to the hydrogen iodide formed during the reaction.

249. "Studies in Phototropy and Thermotropy. Part I. Arylidene- and Naphthylidene-amines." By ALFRED SENIER and FREDERICK GEORGE SHEPHEARD.

In a recent paper the authors described a series of Schiff's bases (salicylidene-amines), one of which, namely, salicylidene-*m*-toluidine, was found to be highly phototropic (*Trans.*, 1909, xcv., 441). The investigation has now been extended to the study of a number of other salicylidene-amines and related compounds, and five compounds, including salicylidene-*m*-toluidine, which exhibit phototropy have been prepared.

Early in this investigation it was observed that many of the coloured bases became deeper in colour on heating, and that this change, like phototropy, was reversible. The whole of the compounds in question were then subjected to an examination to obtain further evidence, if possible, of this property. Their colour changes were noted (1) between the ordinary temperature and a temperature just below their melting-points; and (2) between the ordinary temperature and that of solid carbon dioxide. This led to the interesting fact that most of the compounds exhibit this phenomenon, which has long been known, in isolated instances, among inorganic substances. This reversible change of colour the authors propose to term *thermotropy*.

Whilst it is possible that phototropic and thermotropic isomerism may be explained by intramolecular rearrangement, as is generally supposed, it seems more probable, bearing in mind that the substances affected are solids, that it depends on different modes of aggregation of the ordinary molecules which may be supposed to be grouped together in the probably much more complex molecules of solids.

250. "The Action of Mercaptans on Acid Chlorides. Part I. Oxalyl Chloride: the Mono- and Di-thio-oxalates." By HUMPHREY OWEN JONES and HUBERT SANDERSON TASKER.

The following esters of dithio-oxalic acid have been prepared by the action of oxalyl chloride on the corresponding mercaptans or their metallic derivatives. *Phenyl dithio-oxalate*, a sulphur-yellow solid, melting at 119–120°, and distilling undecomposed. *Methyl dithio-oxalate*, pale yellow prisms, melting at 82.5–83.5°. *Ethyl dithio-oxalate*, yellow prisms, melting at 27–27.25°, and distilling at 235°. *Propyl dithio-oxalate* and *amyl dithio-oxalate*, yellow liquids, the former distilling at 158°/15 mm., and the latter at 206°/19 mm.

On boiling these esters with an alcoholic solution of potassium hydrosulphide, the mercaptan is set free, and *potassium dithio-oxalate* (KSCO)₂, separates as a white crystalline powder. This salt can be used as a delicate test for nickel or cobalt, owing to the formation of a complex potassium nickelo- or cobalto-thio-oxalate, which is intensely coloured. The nickel salt is less stable towards potassium cyanide and strong acids than the cobalt salt, so that by adding potassium cyanide the colour of the nickel salt can be destroyed before that of the cobalt salt, and in this way 10 per cent of cobalt can be detected in the presence of 90 per cent of nickel. The colour of the nickel and cobalt salts can be seen readily at dilutions of 1 in 40,000,000 on looking through 25 cm. of solution.

251. "The Action of Mercaptans on Acid Chlorides. Part II. The Acid Chlorides of Phosphorus, Sulphur,

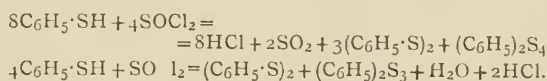
and Nitrogen." By HUBERT SANDERSON TASKER and HUMPHREY OWEN JONES.

Phosphorus trichloride reacts with phenyl mercaptan or its metallic derivatives to give triphenyl trithiophosphite as stated by Schwarze; phosphoryl chloride similarly gives triphenyl trithiophosphate, melting at 115° (Schwarze gave the melting-point as 72°, and this was corrected by Michaelis).

Sulphuryl chloride in the cold gives a deep yellow colour, probably due to the formation of an ester, which disappears with the formation of phenyl disulphide and the evolution of sulphur dioxide.

Thionyl chloride also gives a yellow colour in the cold, but this again disappears quickly; phenyl disulphide is formed and sulphur dioxide is evolved, but the possible new oxide of sulphur, SO₂, is not formed.

Numerous experiments were made to discriminate between the two following equations to represent this reaction:—



It was found that both reactions seem to take place simultaneously, but that the main reaction appears to be represented by the first equation.

Nitrosyl chloride reacts readily with mercaptans in the cold; hydrogen chloride is evolved, and brilliant red colours are produced (probably due to the formation of esters of thionitrous acid), which gradually disappear with the evolution of nitric oxide and the formation of alkyl disulphide. The same colour is produced by the action of the chloride on the mercaptides. When nitrosyl chloride is treated with an alkyl mercaptan at a low temperature (solid carbon dioxide and ether), a small quantity of hydroxylamine hydrochloride is always formed.

252. "The Colouring Matters of the Flowers of Hibiscus sabdariffa and Thespesia lampas." By ARTHUR GEORGE PERKIN.

The flowers of the *Hibiscus sabdariffa* yielded 0.36 per cent of a mixture of three yellow colouring matters, the main constituent of which, C₁₅H₁₀O₈, crystallising in yellow needles, gives an *acetyl* derivative, C₁₅H₄O₈(C₂H₃O)₆, m. p. 229–230°, and, on fusion with alkali, protocathechuic acid. It was identical with gossypetin present in Indian cotton flowers (*Gossypium herbaceum*), the formula, C₁₆H₁₂O₈, previously given for which is now abandoned. Together with quercetin, the flowers yielded a trace of a sparingly soluble new colouring matter, for which the name *hibiscetin* is proposed; this melts at about 340°, and gave a colourless *acetyl* compound, m. p. 238–239°. In addition to these substances, free protocathechuic acid was also isolated. The flowers of *Thespesia lampas* gave quercetin to the extent of 0.6 per cent, together with a small quantity of free protocathechuic acid.

253. "The Reduction of 4-Hydroxy-*o*-toluic Acid." By OSCAR BAUDISCH, GILBERT STANLEY HIBBERT, and WILLIAM HENRY PERKIN, jun.

By reducing 4-hydroxy-*o*-toluic acid with sodium and alcohol, the authors have obtained the four possible isomerides, namely, the two *cis*- and the two *trans*-1-methylcyclohexan-4-*ol*-2-carboxylic acids, of which various derivatives were described. 1-Methyl-Δ⁶cyclohexen-4-*ol*-2-carboxylic acid is also formed in this reaction.

254. "The Reduction of 6-Hydroxy-*o*-toluic Acid." By OSCAR BAUDISCH and WILLIAM HENRY PERKIN, jun.

On reduction with sodium and alcohol, 6-hydroxy-*o*-toluic acid yields a mixture of *cis*- and *trans*-1-methylcyclohexan-6-*ol*-2-carboxylic acid.

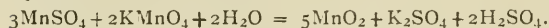
255. "The Reduction of 5-Hydroxy-*m*-toluic Acid." By ANDREW NORMAN MELDRUM and WILLIAM HENRY PERKIN, jun.

By reducing 5-hydroxy-*m*-toluic acid with sodium and isoamyl alcohol, the authors have prepared *trans*-1-methyl-

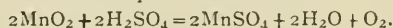
cyclohexan-5-ol-3 carboxylic acid. This is converted into the corresponding *cis-acid* by distillation and hydrolysing the resulting lactone.

256. "The Reaction between Potassium Permanganate and Manganese Sulphate in Acid Solution." By ANUKUL CHANDRA SIKKAR and JATINDRA MOHON DUTTA.

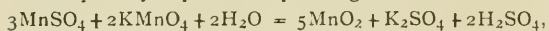
The authors find that in neutral or very faintly acid solution at 85° the reaction between potassium permanganate and manganese sulphate is in accordance with the equation—



In solution freely acidified with sulphuric acid at 85° the reaction is practically the same as in neutral or faintly acid solution; at 100° the manganese dioxide which has been formed by the interaction between the permanganate and manganese salt is attacked by the acid of the solution, forming a certain quantity of manganese sulphate in accordance with the equation—



The manganese sulphate thus formed reacts with a further quantity of potassium permanganate—



and these two reactions occur in a cycle indefinitely, or so long as the solution remains freely acid.

In solutions which were at the start neutral, a certain amount of sulphuric acid is at first produced, but this subsequently becomes used up, and thus in this case a limit is put to the amount of permanganate reduced by a limited quantity of manganese salt even at 100°.

This investigation offers an explanation of what might be termed the catalytic reduction of potassium permanganate in freely acid solution by either manganese salt or manganese dioxide.

257. "The Condensation of Ketones and Aldehydes with the Sodium Derivative of Ethyl Cyanoacetate." Part II. By HENRY DENT GARDNER, jun., and WALTER NORMAN HAWORTH.

An account was given of the investigation of the products formed by the condensation of ethyl sodiocyanoacetate with acetone, methyl ethyl ketone, methyl propyl ketone, diethyl ketone, and methyl hexyl ketone.

PHYSICAL SOCIETY.

Ordinary Meeting, November 12th, 1909.

Dr. C. CHREE, F.R.S., President, in the Chair.

A PAPER entitled "The Absorption Spectrum of Potassium Vapour" was read by Mr. P. V. BEVAN.

The method of studying the absorption spectrum was that used first by Roscoe and Schuster, and of late years elaborated by Prof. R. W. Wood. The fact that the optically dense vapour has really very small density makes it possible to heat the metal in a tube, and to have enough vapour to show strong absorption of light with very little actual distillation to the colder parts of the tube. A tube with quartz plate ends can thus be used and the absorption spectrum studied with a quartz spectrograph. The most evident feature of the spectrum thus obtained is the appearance of the lines of the Principal Series. None of the lines of the two associated series appear, but additional channelled space spectra which are unrepresented in the emission spectra. Fifteen new lines have been obtained in the principal series by this method.

In the invisible region there appears a channelled space spectrum in the red. This shows definite edges of bands towards the violet end of the spectrum. The wave-lengths of the edges of these bands were measured. When the ratios of these wave-lengths to that of the first member of the principal series are found, the values are found to be in the same range as the corresponding ratios as deduced

from Wood's measurements on sodium absorption. This the author regards as evidence of connection between the channelled space spectrum and the principal series of lines. Anomalous dispersion takes place at the first four members of the principal series, but the amount of the effect rapidly diminishes with the order of the line. The remarkable feature of this absorption spectrum and also that of sodium as examined by Wood, is the enormous difference in the properties of the principal series lines from those of other lines in the emission spectrum. Some of these other lines are in emission spectra far stronger than the higher members of the principal series, yet they do not appear at all in the absorption spectrum. This may indicate that the metallic vapour at the comparatively low temperature of these experiments is in quite a different molecular state from its state in a spark or flame, or that in these latter cases chemical action is going on and the emission spectrum is not a simple elementary spectrum.

Dr. J. A. HARKER remarked that in studying the absorption spectrum of a substance by heating it in a tube closed at the ends, there is a region of fog at the ends of the vapour for which allowance should be made. You do not get the absorption spectrum of the vapour because the result is affected by the scattering produced by the particles in the fog.

Prof. C. H. LEES asked if the author could state the nature of the absorption in the second and third series.

Mr. FAYNER asked if there was any difficulty in getting the metal pure. He also asked if the author could state approximately the temperature of the vapour, and whether there was any gas present in the tube.

Prof. BEVAN, in reply, stated that he had observed no evidence of scattering, such as would be produced by the existence of fog in the tube. The amount of vapour used was very small, and therefore there could be little cloud effect. The temperature of the vapour was below the boiling-point of potassium. With regard to the gas in the tube, he had tried hydrogen at atmospheric pressure and at low pressure, and he had also used a vacuum. With regard to the purity of the metal the sodium lines did not appear but they were easily recognised.

A paper entitled "Some Further Notes on the Physiological Principles underlying the Flicker Photometer" was read by Mr. J. S. DOW.

In this paper the author suggests that something may be learned regarding the physiological phenomena governing the flicker photometer by observing whether it is subject to certain physiological effects, such as the "yellow spot" and "Purkinje" phenomena, which are a cause of uncertainty in heterochromatic photometry undertaken with instruments of the ordinary "Equality of Brightness" class.

Some experiments are described which show that the effects referred to do occur, but are apparently much less marked; the question arises why this should be the case. The author suggests a possible explanation based on the assumption that the rod-elements on the retina, in addition to the distinguishing peculiarities attributed to these organs as regards the perception of light and colour, also differ from the "cones" in the fact that they seem to receive a luminous impression more slowly, and retain it longer than these organs; in other words, the "last" of an undiminished luminous impression is longer.

This additional peculiarity is of little consequence in an ordinary photometer of the equality of brightness type, but may possibly play a part in the flicker instrument; it seems to explain why certain effects should be more clearly perceived in one case than in the other.

According to this theory we may imagine the flicker effect to be due to two distinct portions, received by the agency of the rods and cones respectively. Under certain conditions the speed of a flicker photometer may be supposed to be suitable for the use of a "cone-flicker" but too high for the "rod-flicker," which becomes fused into a steady luminous impression and thus does not affect the readings of the instrument.

Some other physiological effects, such as the existence of a recurrent image, seem in harmony with the above view. These matters are, however, still the subject of much dispute between physiologists, and the author regards his experiments as being essentially of a suggestive character requiring more detailed examination. In addition, it is urged that one must be cautious in seeking to draw deductions from cases of colour-blindness, as many different varieties of this affliction exist; thus in some cases colour-blindness is apparently attributable to some disturbance of the centre of perception in the brain, rather than to any peculiarity of the retina.

Dr. EDRIDGE GREEN expressed his interest in the paper, and stated that he was prepared to agree with the effects described, although he thought they were capable of explanation by another theory. The theory of Von Kries was relied upon because the rods contained visual purple while the cones did not. Light falling on the eye liberates visual purple, photochemical action is set up, and nerve sensation results. The speaker described the theory he favoured for the explanation of colour-blindness.

Mr. A. P. TROTTER, after referring to the doubtful value of the flicker photometer for industrial purposes, said that the present investigation should be considered as a scientific one. In discussing the effect of varying the distance of the photometer from the eye, Mr. Dow was really dealing with the angle subtended or the angle of the field of view, and it would be better to use this method of expressing the relation, for it could then be referred to definite parts of the retina. Sir W. Abney and others had mapped the areas of the retina and had found boundaries of colour perception. Abney considers the angles subtended at the centre of curvature of the retina, and his smallest boundary lies within about 15 degrees from the centre, or, according to usual convention, a field of view of about 30 degrees. The whole of Mr. Dow's present experiments fall well within this, and do not extend to the peripheral parts of the retina. Taking the width of the Joly blocks as 2 cm., his starting-point 10 cm. is equivalent to a field of view of about 11 degrees, and his 40 cm. to about 2½ degrees. For the purpose of investigating the action of the peripheral parts of the retina, a photometrical device covering a large field of view should be used, and the middle part should be blocked out.

Dr. RUSSELL suggested that possibly mechanical vibrations are set up in the rods and cones of the eye. These oscillations having probably different periods might explain some of the curious phenomena that Mr. Dow had shown to the meeting. The cones in the eye did not satisfy the mathematical definition of a cone, and it would be extremely difficult to make any calculations. He was not convinced that the rods were unable to perceive colour. According to the theory advanced at threshold illumination only the rods are active. Dr. Burch has shown that after the eye is rested its sensitiveness to the more refrangible rays is greatly increased. In this case, at threshold illumination, when presumably only the rods are active, the sodium lines appear to be green. The rods therefore at low illuminations perceive green, and so the assumption that they do not perceive colour is inadmissible.

Mr. C. C. PATERSON expressed his great interest in the paper, and appreciation of the experimental skill shown by the author. He said he wished to make some observations on the so-called yellow-spot effect, because, whilst being able to offer no well substantiated theory to account for the phenomena which Mr. Dow had observed, he could not altogether make the application of the rod and cone theory in this instance agree with the experimental facts. Considering the interesting lower diagram on page 3, there was a curve there which showed that a 40 per cent difference was obtained in the contrast between two surfaces illuminated by a red and a green light respectively, according to whether the observer's eye was 20 or 60 centimetres away from the surfaces. The author explained this difference by assuming that in one case more of the retina was employed than in the other, so that in the 20 centi-

metre case a ring of the retina surrounding the yellow spot and containing more rods, was being used. Referring to the top left hand patch in Figure 3, it might be noted that at 20 centimetres distance a square which just included the words "red" and "green" was the area which approximately covered the yellow spot, if the eye were directed on the centre of the figure. At 60 centimetres distance the whole height of the figure about covered the yellow spot. If Mr. Dow's explanation were correct it meant, as far as he could see, that as he obtained a balance and looked at the centre of his patches from 20 centimetres distance, the author must have been conscious of at least a 40 per cent difference between the comparison at the centre and the comparison at the top or bottom of the two illuminated areas. It was difficult to understand how balance could be obtained if this condition existed, and Mr. Trotter's suggestion of blocking out the centre of the patch and observing only the boundaries seemed to be a valuable one. He did not think that in making comparisons the area of the retina outside the yellow spot was used to any appreciable extent. All who were in the habit of using photometers were probably conscious that if they kept the eye fixed, only a small area of the illuminated surfaces was being considered by the observer at one moment, and the sensation from the outlying area of the surface had no appreciable weight compared with that from the centre, on to which the eye was directed. He (Mr. Paterson) was inclined to believe that many of the discrepancies of photometric comparisons were due as much, if not more, to psychological than to physiological causes. He did not see why the retina should be regarded as the only faulty link in the chain. In the latter portion of the paper in which the flicker question was discussed, the author showed the observed facts to be very well explained by the theory of the rods and cones, and he congratulated him upon the flicker experiment which he had shown.

Mr. RAYNER referred to the use of a Ritchie wedge as a flicker photometer, and asked if there was a greater intensity at the edges of the field due to some direct reflection.

Mr. J. S. DOW, replying to Dr. Edridge Green's remarks, said that he quite recognised that the theory of the action of the retina was a matter for physiologists to deal with, and he was much interested in Dr. Edridge Green's explanation of the most recent view. His suggestions regarding the flicker photometer were intended to bring these phenomena into line with the well authenticated other physiological effects which the rod and cone theory had served to explain so completely. He quite appreciated the importance of Dr. Edridge Green's discovery of visual purple in the fovea. Mr. Trotter's suggestion regarding expressing results in angles subtended at the eye was a good one: in leaving the results in their present form he had merely wished to give an idea of conditions occurring in an actual photometer. For experimental purposes, however, it was often desirable to use a larger retinal area. Mr. Trotter's suggestion that the centre part of the retina should be blocked out was diametrically opposite to that of M. Blondel, who had suggested using *only* the centre part of the retina, where cones only exist. As a principle in photometry, however, it seemed desirable not to depart further from the condition of the eye in practice than could be avoided. Dr. Russell had criticised the suggestion that the rods could not distinguish colour, but yet were most sensitive to blue-green light. As he understood the theory, it seemed to be suggested that the perception of "luminosity" might be greatest for light of this wave-length, although the rods could not analyse colour, *i.e.*, all qualities of light appeared to them white. Dr. Burch's experiments, however, had apparently shown that after resting in the dark for two hours or more, it was possible to distinguish colours as long as any light was visible at all; this result certainly seemed at variance with the above view of the behaviour of the rods, and in itself suggested that the theory required modification. In reply to Mr. Paterson's point, he might say that in viewing a

coloured surface he was not conscious of any want of uniformity in brightness due to retinal peculiarities; the eye seemed to weigh up the appearance as a whole, just as in the case of white light. No doubt psychological influences played some part in all these problems; however, the existence of the yellow spot and Purkinje effects had been known for a long time and both effects had been authenticated by many observers. It was only the explanation that seemed still a matter for conjecture.

Dr. EDRIDGE GREEN exhibited a "*Colour-perception Spectrometer*."

This instrument has been designed for testing colour-perception. It consists of an ordinary spectrometer with a single prism, fitted with two wave-length drums which work two shutters placed in the focal plane of the eyepiece. By means of the shutters any part of the spectrum can be viewed at will and the wave-lengths of the edges of the patch under observation can be read off from the drums. Dr. Edridge Green described how the instrument is used for testing colour-blindness, and referred to the superiority of the method over those usually adopted.

A paper entitled "*Tables of the Ber and Bei and Ker and Kei Functions, with further Formulae for their Computation*," by Mr. H. G. SAVIDGE, was taken as read.

NOTICES OF BOOKS.

A Manual of Forensic Chemistry dealing especially with Chemical Evidence, its Preparation and Adduction. By WILLIAM JAGO, F.I.C., F.C.S., Barrister-at-Law. London: Stevens and Haynes. 1909.

This book will be of the greatest value to two classes of readers—public analysts and chemists who are required to explain the results of tests performed by them, and the deductions to be drawn, in language which can be readily understood without any technical knowledge, and lawyers who have to determine the value of the evidence given by the chemist. Both classes, especially perhaps the latter, have to perform difficult tasks which they will find greatly facilitated by a study of this book. Certain aspects are treated very fully, and reports of typical illustrative cases are given, with notes calling attention to important points. The author has much information to give relating to the giving of evidence in both civil and criminal cases, and in addition his discussions of the more scientific side of such questions as the permissibility of the use of colouring matters and preservatives in articles of food are marked by a wide knowledge and an impartial judgment. The text is based upon a course of lectures recently delivered at University College, London, with some additions to make the treatment of the subject more complete.

OBITUARY.

THE LATE DR. WILLIAM JAMES RUSSELL, F.R.S.

THE announcement of the death of Dr. W. J. Russell, F.R.S., which was made in the CHEMICAL NEWS last week, will have been read with much sincere regret; it would be difficult to over-estimate the value of his influence over the students who attended his lectures, and who were inspired and constantly encouraged by his enthusiastic teaching, while on all sides his power of organisation and his zeal for scientific work will be much missed.

Born at Gloucester in 1830 he received his early education at Bristol and Birmingham, and entered upon his college career in 1847 at University College, London, where Graham was then Professor of Chemistry. He subsequently went to Heidelberg to work under Bunsen. Upon returning to England he became Professor of

Chemistry at Bedford College, then at St. Mary's Hospital, and finally at St. Bartholomew's Hospital Medical School, resigning the last post in 1897. His tireless energy would not allow him to take a rest after the cessation of his professorial duties, but he continued his research work, up to within a very short time of his death, at the Davy-Faraday Research Laboratory of the Royal Institution.

Some of his most important original work related to improvements of methods of analysing gases, which he studied in collaboration with Dr. A. W. Williamson. He also spent much time upon the determination of the atomic weights of nickel and cobalt, while more recently he had been investigating the action of certain radiations upon the photographic plate. He published a most important paper upon the production of absorption bands by colourless liquids, as well as many studies in photographic chemistry, in which he took a specially keen interest.

In addition to his teaching and research work, he took an active part in the organisation and management of various learned societies which recognised his powers and gratefully accepted his willing services. Thus he was a Fellow of the Chemical Society and a member of its Council, and a Fellow of the Institute of Chemistry, and President from 1894 to 1897. He was elected a Fellow of the Royal Society in 1872, and subsequently served on its Council, becoming Vice-President in 1899. He held various examining posts in connection with the University of London and the Science and Art Department of the Board of Education, and was a member of the Council of Bedford College, London. His rare combination of qualities won for him the sincere regard and affection of all with whom he came in contact, and the scientific world will join with his many personal friends in sorrow for his loss.

NOTES AND QUERIES.

* * * Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Ultra-violet Light.—Is this visible to some eyes? On October 7 I had an opportunity of viewing a particularly fine rainbow, due east at 3 p.m., with the sun declining, as far as I could form an opinion, almost due west. Beyond the ordinary dark blue of the spectrum the violet band was particularly impressive, formed a quite broad band relatively to the blue, and beyond this a shimmering band of glowing white. J. C. T.

MEETINGS FOR THE WEEK.

MONDAY, 29th.—Royal Society of Arts, 8. (Cantor Lectures). "Aeronautics," by C. C. Turner.

TUESDAY, 30th.—Royal Society of Arts, 4.30. "Agricultural Development in Nyasaland," by S. Simpson.

WEDNESDAY, Dec. 1st.—Royal Society of Arts, 8. "Improvements in Resilient Wheels for Vehicles," by the Hon. R. C. Parsons.

Society of Public Analysts, 8. "Composition of Cream," by R. R. Tatlock and R. T. Thomson. "Analyses of Vulcanised Rubber Goods," by C. Beadle and H. P. Stevens. "Gravimetric Estimation of Nickel in Nickel Steel," by E. L. Rhead. "The Milk Supply of Two Large Towns," by F. W. F. Arnaud and E. Russell.

THURSDAY, 2nd.—Chemical, 8.30. "New Method for the Detection of Sodium, Calcium, and Rubidium," by W. C. Ball. "Correction of the Specific Gravity of Liquids for the Buoyancy of Air," by J. Wade and R. W. Merriman. "Synthesis with the Aid of Monochloromethyl Ether—Part II. Action of Monochloromethyl Ether on the Sodium Derivative of Ethyl Acetoacetate," by J. L. Simonsen and R. Storey. "Synthesis of Hordenine, the Alkaloid from Barley," by G. Barger. "Note on Dr. Scott's Paper on 'The Molecular Weight of Tetra-ethyl Ammonium Bromide and the Atomic Weight of Carbon,'" by Sir Edward Thorpe. "Relation between the Chemical Constitution of Mono-azo Dyes and their Fastness to Light," by E. R. Watson, A. C. Sirkar, and J. M. Dutta. "Synthesis in the Epinephrine Series," by F. Tutin, F. W. Caton, and A. C. O. Hann.

THE CHEMICAL NEWS.

VOL C., No. 2610.

ON THE ELECTRO-ANALYTICAL DETERMINATION OF LEAD AS PEROXIDE.*

By HENRY J. S. SAND, Ph.D., D.Sc.

THE electro-analytical determination of lead as peroxide has hitherto been rendered somewhat uncertain by the fact that when dried at temperatures at which it may be considered to be free from the risk of decomposition, it is always found to retain a small amount of water, and the corrections which various investigators state should be made for this vary very considerably. It has therefore been proposed by Treadwell to ignite the peroxide at a dull red heat, and thus convert it into oxide ("Analytical Chemistry," New York, 1904, ii., 140). This suggestion can, however, be carried out conveniently only when a dish is employed as the anode. Where gauze electrodes are made use of, it has been found practically impossible to effect the conversion in a gas flame without at the same time obtaining some lead as metal, owing to the reducing action of the flame.

The theoretical factor for the calculation of lead from peroxide is 0.866, and the experimentally found factors which various investigators have put forward vary between 0.853 to 0.857 according to Holland and Bertiaux (*Analyse par Electrolyse*, 1906, 72 and 173), and 0.8634 to 0.8643 according to R. O. Smith (*Journ. Am. Chem. Soc.*, 1905, xxvii., 1287), and also according to Arthur Fischer and Vossen (Arthur Fischer, *Elektroanalytische Schnellmethoden*, 1908, 174; or Classen, *Elektroanalyse*, 1908, 5th ed., 125). The results thus differ from the theoretical value according to the investigator, by amounts varying between 0.15 and 1.5 per cent. The slight variations found by the same investigator refer to different amounts of lead. The temperatures for drying are given variously by the different investigators as 200° and 200° to 230°, but it may be considered certain that the discrepancies are not due, in the main, to difference of temperature.

The following experiments were carried out primarily with the view to elucidate the behaviour of a lead peroxide deposit on drying, and incidentally further to study the effect of varying conditions on its nature generally.

The circumstances controlling the coherence of the peroxide have been found very similar to those which govern the coherence of metal deposits. The higher the temperature and the smaller the current density, the more coherent is the precipitate. When employing the conditions which are most favourable to the quality of the deposit, it is, however, necessary to avoid too large an amount of nitric acid in the electrolyte, and it is specially important to remove any oxides of nitrogen which may be present by evaporating the electrolyte to dryness before a determination. Even small quantities of these oxides will render the exhaustion of the electrolyte at high temperatures impossible. The temperature was always kept slightly below the boiling-point, a maximum of about 97° never being exceeded, as the current appears to produce lower oxides of nitrogen from the nitric acid at 100°.

Large quantities of ammonium nitrate appear to render the precipitate of peroxide loose. It is not improbable that, under suitable conditions, alkali plumbates, and even the plumbates of heavy metals, may sometimes be formed as intermediate products. (This may explain some of the abnormal results recently obtained by G. Vortmann, *Ann. Chem.*, 1907, cccli., 283).

Colloids appear to have a similar effect on the deposits of lead peroxide as on those of metals. When obtained

from a solution in which a small amount of stannic acid in the colloidal state is present, the precipitate of lead peroxide is always much more coherent than it would otherwise be. Small amounts of the colloid are precipitated with the peroxide. This fact should also be borne in mind when a solution is to be electrolysed in which colloidal metal oxides may be produced by the hydrolysis of salts (see Note above regarding Vortmann's results).

In almost all the experiments to be described, the electrolyte contained only nitric acid beside the lead salt. In two or three a small amount of nitric acid and a very large amount of copper nitrate were, however, added in conformity with the suggestion by Holland and Bertiaux (*loc. cit.*, p. 71). The method was, however, not proceeded with further, as it suffers from the fact that the electrolyte cannot be conveniently tested for freedom from lead, and besides, the results were found two or three tenths of a per cent higher than with the strongly acid electrolyte free from copper.

The electrodes employed were those previously described (*Trans. Faraday Soc.*, 1909, v., 159; *Trans. Chem. Soc.*, 1908, xciii., 1572). The outer electrode was always the anode. The gauze covers a surface of about 50 to 55 sq. cm. It consists of about fourteen wires per linear centimetre of approximately 0.2 mm. diameter, and the total surface available for the peroxide is probably somewhat less than 90 sq. cm. The volume of the liquid was about 85 cc. The exhausted electrolyte was always tested for absence of lead by neutralising a sample with ammonia and adding hydrogen sulphide, and the cathode was also examined for freedom from lead.

In a former paper (*Trans. Chem. Soc.*, 1907, xci., 397) the author gave some results for the determination of lead as peroxide. The theoretical factor was employed, and both positive and negative deviations were obtained, the former seldom exceeding 0.3 per cent. The details of the method of drying, which were at that time not given, may here be stated. An oven improvised from a one and a-half litre Jena beaker, protected at the bottom by asbestos-paper, was employed, which was covered by a cork lid, and a current of air was drawn through by means of a water-pump.

In the course of the present investigation it was soon found that at a temperature of about 200° a lead peroxide deposit is capable of absorbing moisture in a damp atmosphere, and only parts with this exceedingly slowly when heated in carefully dried air. The apparatus employed for heating in a moist atmosphere consisted of a sheet-iron can of about 25 cm. height and 11 cm. width, which was closed at the top by a cork. The latter was provided with an opening designed to hold a smaller cork, to which the electrode was suspended by a wire. Some water was evaporated at the foot of the can, which contained sufficient openings to allow the steam to escape, but was devoid of any arrangement to produce circulation of the atmosphere. The distance of the electrode from the bottom of the can was about 10 cm. In the experiments the electrode was always removed from the can while hot, so that there might be no possibility for drops of water to condense on it on cooling.

For those experiments in which the electrode was to be heated in dried air, a copper cylinder of about 25 cm. height and 5 cm. diameter was employed. The bottom was brazed on, and the top was closed hermetically by a cork. An altogether unexpected difficulty was experienced in obtaining a flawless cork of the necessary diameter cut at right angles to the grain which would fit gas-tight. This difficulty was only overcome by obtaining a cork cut from a composite piece, consisting of three parts glued together. The cork held two glass tubes by means of which air previously dried in a tower containing caustic potash and calcium chloride could be caused to circulate with the aid of a water-pump.

In one experiment the electrode, with about 0.37 gm. of lead peroxide, was heated to 200° in the moist atmosphere for twenty-five minutes, whereupon it gained 1.1

* A Paper read before the Faraday Society, November 30, 1909.

mgram. in weight. On further heating in the dried air for fifty minutes at 180° , it lost 0.5 mgram., and on again heating in the dry air for over an hour, it lost 0.3 mgram. After this it increased in the moist air at 200° in fifteen minutes by 2 mgrms., in another twenty minutes under the same conditions by 1.3 mgram., then again in twenty-five minutes by 1.5 mgram., then in twenty minutes by 0.4 mgram., and in another twenty minutes by 0.8 mgram., making a total increase of 6 mgrms., *i.e.*, of about 1.7 per cent. After this the increase on further heating was inappreciable. The heavy deposit thus obtained only parted with its water exceedingly slowly when heated in the carefully dried atmosphere. In twenty minutes it lost 0.8 mgram. at about 210° , and even at much higher temperatures the decrease was very slow; thus the loss in an hour at 230° to 240° was only 0.6 mgram., and at about 280° in an hour and a half it was 1.4 mgram.

These experiments show that in drying the peroxide it is specially important not to allow it to absorb water from a moist atmosphere at a high temperature. They furnish a quite sufficient and satisfactory explanation why different investigators should have obtained different results when special precautions were not taken to remove the moisture from the atmosphere of the drying oven. At a minimum temperature of about 230° it appeared that even in a damp atmosphere no appreciable increase took place, but attention must here be drawn to the impossibility to heat an object of 5 or 6 cm. height uniformly in an ordinary drying oven. A difference of 20° to 30° must always be allowed for between the hottest and the coldest parts of the object. Drying at a maximum temperature of 300° was also tried, but it appears that the peroxide is not absolutely stable at these high temperatures, and that a continual decrease in weight takes place. The author believes that it may be taken as certain that when lead peroxide is in contact with air, there is no true equilibrium which would condition the existence of a definite temperature of decomposition, *i.e.*, a temperature at which the decomposition tension of the peroxide would be equal to the partial pressure of the oxygen contained in the atmosphere. We are, on the contrary, here no doubt dealing with a so-called false equilibrium for which it would be exceedingly difficult to state definite conditions of stability.

All these circumstances will always tend to make the drying of the peroxide at high temperatures a somewhat uncertain operation. The best conditions are no doubt to take the deposit quickly up to a temperature of about 230° in a current of dried air. The factor which was found at a temperature of 200° in dried air varied between 0.863 and 0.865.

A much more simple and probably also more certain method to obtain satisfactory results was afterwards discovered in adopting the identical procedure always made use of for metals, *viz.*, to dip the electrode first into a jar containing alcohol, then into another containing ether, and then to dry it rapidly over a Bunsen burner. The electric current itself is made use of to keep the deposit free from water by electric endosmose. The conditions for securing a satisfactory result are a high temperature of the electrolyte and a high current density. (The dehydrating action of the current by electro-osmose especially at high temperatures has been made use of for the dehydration of peat—Höchstler Farbwerke D.R.P., 179,985 kl. 82a. and D.R.P. 185,189 kl. 82a). A special experiment showed that a lead peroxide precipitate does not absorb water so rapidly that an increase of weight need be feared during the operations of disconnecting. The electrode with a dried weighed precipitate of 0.4600 gm. lead peroxide was dipped into water and dried with alcohol and ether. The operations were repeated, and in both cases no change of weight was observed. It was likewise shown that no error need be feared if the ether should burn for an instant after accidental ignition during the process of drying. The effect of varying conditions of temperature and current on the weight of the precipitate is shown in Table I. A measured quantity of solution containing 0.3172 gm. of

lead was taken for each experiment, the amount of nitric acid was 10 cc. per 85 cc. solution. Small currents were taken at the low temperatures in order to obtain a coherent deposit and to avoid the precipitation of lead on the cathode.

TABLE I.

PbO ₂ found.	Temperature.	Amperes.	Time (mins.)	Factor.
0.3668	92—95°	5	12	0.8648
0.3690	65°	5	9	0.8596
0.3695	40°	0.7	20	0.8585

Table II. gives a summary of the results obtained under slightly varying conditions. In all the experiments, except Nos. 7 and 8, metallic lead was started from and the solution was quite free from oxides of nitrogen as already explained. The amount of nitric acid present was always 10 cc. and the volume of the solution 85 cc. The results may be summarised as follows. For a temperature of about 90° and a current strength of 5 amps. with the electrodes described the factor 0.863 may be taken. For a temperature of 95° to 97° the factor is 0.865. In either case when alloys are analysed in which the percentage of lead is not very high, it will no doubt be sufficiently accurate to employ the theoretical factor 0.866. The amount of peroxide deposited does not appear to have any definite effect on the value of the factor.

TABLE II.

No.	Pb taken.	PbO ₂ found.	Amperes.	Temperature.	Time (mins.)	Factor.
1.	0.3194	0.3699	5	90	10	0.8635
2.	0.3882	0.4499	5	90	9	0.8629
3.	0.3970	0.4600	5	93	—	0.8630
4.	0.3656	0.4228	5—10	92—95	12	0.8647
5.	0.3830	0.4431	5	92—97	15	0.8644
6.	0.3626	0.4205	5	90—97	15	0.8623
7.	1.0200	1.1794	5	90—97	20	0.8649
8.	0.95100	1.1022	5	95—97	20	0.8627
9.	0.95100	1.1007	5	95—85	35	0.8640
10.	1.0232	1.1831	5	95	20	0.8649
11.	1.0847	1.2542	5	97—80	17	0.8648
12.	0.1214	0.1407	5	96—75	9	0.863

A NEW RAPID VOLUMETRIC METHOD FOR THE DETERMINATION OF NIOBIUM IN THE PRESENCE OF TANTALUM, AND ITS APPLICATION TO THE ANALYSIS OF NIOBIUM MINERALS.*

By F. J. METZGER and C. E. TAYLOR.

(Concluded from p. 259).

Analysis of Minerals.

THE method was next applied to the analysis of minerals, and for comparison the minerals were also analysed by the fractional crystallisation method, details of which follow.

Crystallisation Method.—Fuse 1 to 2 grms. of the mineral with eight to ten parts of potassium bisulphate. Boil with water until completely disintegrated, and filter, using a rubber funnel. Wash with hot water until the washings give only a faint test for sulphates. Wash on the funnel with several portions (15 or 20 cc. each), of yellow ammonium sulphide, hot, mixing on the filter as much as possible to get the best action. Wash with hot water until free from ammonium sulphide, then with dilute sulphuric acid to remove iron sulphide, then with hot water to remove sulphuric acid (the residue on the filter-paper should now be pure white, and contain nothing but silica, niobic and tantallic acids). Dissolve through the filter by means of warm dilute hydrofluoric acid. (Any dark

* From the *School of Mines Quarterly*, xxx., No. 4.

coloured residue indicates incomplete decomposition of the mineral, and the residue must be ignited, fused, and treated as before).

Add potassium fluoride approximately equivalent in weight to that of the sample taken. Evaporate on a water-bath until the mass just solidifies on cooling. Dissolve in the smallest possible quantity of boiling hot water. Set aside to crystallise. The tantalum crystallises as K_2TaF_7 , in the form of needles. The niobium crystallises as $K_2NbOF_5 \cdot H_2O$, in the form of plates. These crystals must be carefully examined, using a magnifying glass if necessary, to determine whether they are needles or plates, or both. The first crop of crystals is nearly always needles, *i.e.*, free from niobium. If there are no plates, filter on a small paper, using a rubber funnel, catching the filtrate in a platinum dish, and wash sparingly with water slightly acidified with hydrofluoric acid, and containing about 1 grm. of potassium fluoride per 100 cc. Evaporate the filtrate to dryness exactly as before, take up in boiling water, &c., filtering off the needles (if free from plates) through the same funnel used for the first crop of crystals. This operation is repeated until a crop of crystals is obtained which consists of a mixture of needles and plates. When this mixture is obtained, add gradually a little of the wash-water (1 or 2 cc. at a time), stirring until the plates disappear. Filter off the needles as before, and wash sparingly with the washing solution. The filtrate should now contain all of the niobium, and the crystals on the filter, all of the tantalum as the double fluorides. Dissolve the tantalum salt from the filter, using boiling hot water, and adding a few drops of hydrofluoric acid, the latter being necessary to prevent the formation of an insoluble tantalum compound. Add sulphuric acid to both the niobium and tantalum portions, and evaporate to copious fumes of SO_3 to remove fluorides, and boil with a considerable amount of water. Each element is precipitated by this boiling as its respective oxide, or hydrated oxide, insoluble in water. Filter, wash with hot water, ignite ten minutes with a blast-lamp, and weigh.

Remarks.—Evaporation of the fluoride solution must be carried on with great care, for if carried too far the salts (especially the tantalum) are apt to become partially decomposed and thereby rendered insoluble in water. If evaporation is not carried far enough, too much hydrofluoric acid remains, which would cause the niobium to crystallise in the form of prisms instead of plates, which are difficult to distinguish from the needles of the tantalum salt.

Volumetric Method.—Fuse from 0.2 to 1.0 grm. of the mineral with 5 to 10 grms. of potassium bisulphate, and proceed in exactly the same manner as with the crystallisation method to the point of dissolving the precipitate from the paper with hydrofluoric acid. To the hydrofluoric acid solution, containing the niobium and tantalum, in a platinum dish, add 10 cc. of concentrated sulphuric acid. Evaporate to copious fumes. Add a few cc. more of sulphuric acid, and repeat the evaporation to dense SO_3 fumes. Allow the solution to cool, and pour into cold water, washing the dish well, and add cold water to a volume of about 500 cc. Heat to boiling, and boil for a few minutes. Filter, wash with boiling water until only a faint test for sulphate. Ignite ten minutes with a strong blast, and weigh. This gives the weight of the combined oxides Nb_2O_5 and Ta_2O_5 . Fuse with 5 grms. of potassium bisulphate. Add 10 cc. of concentrated sulphuric acid, and heat gently to a clear solution. Transfer to a beaker, rinsing out the crucible with 30 cc. of concentrated sulphuric acid. Allow to cool. (Any cloudiness indicates incomplete decomposition of the oxides). Add 2 grms. of succinic acid, and agitate; add about 20 cc. of saturated aqueous solution of succinic acid in a fine stream from a wash bottle, keeping the solution in motion to assist solution of the succinic acid. Add water gradually to a volume of 200 cc., constantly agitating the solution. Heat to $75^\circ C.$, reduce, and titrate as previously described. (See Table VII.).

TABLE VII.

No.	Sample.	Volumetric.		Crystallisation.	
		Nb_2O_5 , per cent.	Ta_2O_5 , per cent.	Nb_2O_5 , per cent.	Ta_2O_5 , per cent.
57.	A	53.52	22.84	57.13	21.09
58.	A	54.06	22.69	56.82	21.30
59.	A	54.42	22.40	—	—
60.	A	54.84	23.08	—	—
61.	B	27.11	54.27	31.63	50.36
62.	B	27.44	53.91	30.24	51.24
63.	C	14.39	67.86	17.85	64.63
64.	C	14.30	68.26	—	64.41
65.	D	17.27	53.21	26.66	43.43
66.	D	16.48	53.92	27.03	43.98
67.	D	16.32	—	—	—
68.	D	16.07	—	—	—

Sample "D" contains quite large amounts of tin, difficult to separate from the niobium and tantalum, as experience has shown. This tin accumulates in the niobium portion in the crystallisation method, thus causing high results for niobium. In the volumetric method the tin has no effect on the determination of niobium, but would cause the tantalum (estimated by difference) to be too high.

Comparison of Volumetric and Crystallisation Methods.

Columbite A was analysed again in triplicate by the crystallisation method. The niobium and tantalum oxides obtained as a result of these analyses were individually fused and analysed for niobium by the volumetric method, giving results shown below.

TABLE VIII.

A. Crystallisation Method.

	No. 84.	No. 85.	No. 86.
Mineral taken ..	0.5873	0.5737	0.5264
Nb_2O_5 found ..	0.3294	0.3198	0.2995
Ta_2O_5 found ..	0.1136	0.1185	0.1080
Nb_2O_5 , per cent ..	56.09	55.74	56.89
Ta_2O_5 , per cent ..	19.35	20.65	20.51

B. Volumetric Method.

	No. 84.	No. 85.
Mineral taken ..	0.5873	0.5737
From Nb_2O_5 portion— Nb_2O_5 found	0.3164	0.3089
From Ta_2O_5 portion— Nb_2O_5 found	0.00289	0.00723
Nb_2O_5 , total ..	0.3193	0.3161
Nb_2O_5 , per cent ..	54.37	55.10

Nb_2O_5 is here shown to be present in the tantalum portion (as obtained by the crystallisation method), and although no direct tests could be applied for the determination of the Ta_2O_5 in the niobium portion, the results of titration show beyond reasonable doubt that it was present.

The average of these volumetric determinations gives 54.73 per cent for Nb_2O_5 , whereas the average of the results obtained by the regular volumetric method is 54.21 per cent Nb_2O_5 , sufficient evidence to show that the results obtained by the crystallisation method are in error.

Conclusions.

1. A potassium sulphate-sulphuric acid solution of niobium and tantalum, to which succinic acid has been added, may be diluted considerably, and heated without precipitation of compounds of either element.

2. The niobium of this solution may be reduced by passing the solution through a Jones reductor, after which the niobium may be determined volumetrically with potassium permanganate solution.

3. Neither the tantalum nor succinic acid are affected by the processes of reduction and oxidation as carried out in this method.

4. The temperature of the niobium solution during reduction should be $75^\circ C.$, and the niobium should be titrated at once, the whole operation being carried out in an atmosphere of carbon dioxide.

5. The degree of amalgamation of the zinc used in the reductor is of great importance, the proportion adopted being 600 grms. of C.P. 20 to 30 mesh zinc to 0.5 gm. of mercury.

6. The method of fractional crystallisation is at best only an approximate separation of niobium and tantalum. Some tantalum remains in solution with the niobium, and a little niobium is held by the tantalum.

7. The volumetric method gives lower results for niobium, and correspondingly higher results for tantalum than the crystallisation method.

8. The volumetric method is not extremely accurate, but is much more accurate than the method of crystallisation, and may be carried out in considerably less time.

9. Under the conditions adopted, the niobium is reduced to a degree indicated by the oxide, $\text{Nb}_2\text{O}_3 \cdot 1.07$ (i.e., 1 cc. of N 10 potassium permanganate solution equals 0.007052 Nb_2O_5).

SOME FORMS OF FOOD ADULTERATION AND SIMPLE METHODS FOR THEIR DETECTION.*

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and
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(Concluded from p. 249).

Edible Oils.—Detection of Cotton-seed Oil.

WITH the exception of cotton-seed oil, the adulterants ordinarily used with edible oils are of such a nature that the experience and training of a chemist and the facilities of a chemical laboratory are essential to their detection. There is, however, a simple test for the detection of cotton-seed-oil, known as the Halphen test, which may be readily applied.

The reader is cautioned that great care must be taken in the manipulation of this test, as one of the reagents employed—carbon bisulphide—is very inflammable. The manipulator should use every possible safeguard, and should see to it that only a small portion of his reagent is exposed at one time. The chemicals employed in the preparation of the reagent used for this test are not household articles. They may, however, be obtained in any pharmacy. The mixture should be prepared by a druggist rather than by an inexperienced person who desires to use it.

In order to perform the test, two or three tablespoonfuls of this reagent are mixed in a bottle with an equal volume of the suspected sample of oil, and heated in a vessel of boiling salt solution (prepared by dissolving one tablespoonful of salt in a pint of water) for ten or fifteen minutes. At the end of that time, if even a small percentage of cotton-seed oil be present, the mixture will be of a distinct reddish colour, and if the sample consists largely or entirely of cotton seed oil, the colour will be deep red.

Eggs.

There is no better method for the testing of the freshness of an egg than the familiar one of "candling," which has long been practised by dealers. The room is darkened, and the egg held between the eye and a light; the presence of dark spots indicates that the egg is not perfectly fresh, one that is fresh presenting a homogeneous translucent appearance. Moreover, there is found in the larger end of a fresh egg, between the shell and the lining membrane, a small air cell which, of course, is distinctly transparent. In an egg which is not perfectly fresh this space is filled, and hence presents the same appearance as the rest of the egg.

It is now a matter of considerable importance to be able to distinguish between fresh eggs and those that have been packed for a considerable time. Until recently that was not a difficult matter. All of the solutions that were formerly used extensively for that purpose gave the shell a

smooth glistening appearance which is not found in the fresh egg. This characteristic, however, is of less value now than formerly, owing to the fact that packed eggs are usually preserved in cold storage. There is now no means by which a fresh egg can be distinguished from a packed egg without breaking it. Usually in eggs that have been packed for a considerable time the white and yolk slightly intermingle along the point of contact, and it is a difficult matter to separate them. Packed eggs also have a tendency to adhere to the shell on one side, and when opened frequently have a musty odour.

Flavouring Extracts.

Although quite a large number of flavouring extracts are on the market, vanilla and lemon extracts are used so much more commonly than other flavours that a knowledge of their purity is of the greatest importance. Only methods for the examination of those two products will, therefore, be considered.

Vanilla Extract. Vanilla extract is made by extracting vanilla beans with alcohol. It consists of an alcoholic solution of vanillin (the characteristic flavouring matter of the vanilla bean) and several other products, chiefly resins, which, though present in but small amount and having only a slight flavour in themselves, yet affect very materially the flavour of the product. Vanilla extract is sometimes adulterated with the extract of the tonka bean. This extract to a certain extent resembles vanilla extract. The extract of the tonka bean, however, is far inferior to that of the vanilla bean. It has a relatively penetrating, almost pungent odour, standing in sharp contrast to the flavour of the vanilla extract. This odour is so different that one who has given the matter some attention may readily distinguish the two, and the quality of the vanilla extract may often be judged with a fair degree of accuracy by means of the odour alone.

Another form of adulteration, and one that is now quite prevalent, is the use of artificial vanillin in place of the extract of either vanilla or tonka beans. Artificial vanillin has, of course, the same composition and characteristics as the natural vanillin of the vanilla bean. Extracts made from it, however, are deficient in the resins and other products which are just as essential to the true vanilla as is vanillin itself. Since vanillin is thus obtained from another source so readily, methods for the determination of the purity of vanilla extract must depend upon the presence of other substances than vanillin.

Detection of Caramel.—The colouring matter of vanilla extract is due to substances naturally present in the vanilla bean and extracted therefrom by alcohol. Artificial extracts made by dissolving artificial vanillin in alcohol contain no colour of themselves, and to supply it caramel is commonly employed. Caramel may be detected in artificial extracts by shaking and observing the colour of the resulting foam after a moment's standing. The foam of pure extracts is colourless. If caramel is present a colour persists at the points of contact between the bubbles until the last bubble has disappeared. The test with fullers' earth given for caramel in vinegar is also very satisfactory, but of course requires the loss of the sample used for the test.

Examination of the Resin.—If pure vanilla extract be evaporated to about one-third its volume the resins become insoluble and settle to the bottom of the dish. Artificial extracts remain clear under the same conditions. In examining vanilla extract the character of these resins is studied. For this purpose a dish containing about an ounce of the extract is placed on a tea-kettle or other vessel of boiling water until the liquid evaporates to about one-third or less of its volume. Owing to the evaporation of the alcohol the resins will then be insoluble. Water may be added to restore the liquid to approximately its original volume. The resin will then separate out as a brown flocculent precipitate. A few drops of hydrochloric acid may be added and the liquid stirred, and the insoluble matter allowed to settle. It is then filtered, and the resin on the filter-paper washed with water. The resin is then

* Bulletin No. 100, Bureau of Chemistry, U.S. Department of Agriculture.

dissolved in a little alcohol, and to one portion of this solution is added a small particle of ferric alum and to another portion a few drops of hydrochloric acid. If the resin be that of the vanilla bean, neither ferric alum nor hydrochloric acid will produce more than a slight change of colour. With resins from most other sources, however, one or both of these substances yield a distinct colour change.

For filtering, a piece of filter-paper should be folded once through the middle, and again at right angles to the first fold. It may now be opened with one fold on one side and three on the other, and fitted into a glass funnel. When the paper is folded in this manner the precipitated resins may be readily washed with water. When the washing is completed the resins may be dissolved by pouring alcohol through the filter. This work with the resins will require some practice before it can be successfully performed. It is of considerable value, however, in judging of the purity of vanilla extract.

Lemon Extract.—By lemon extract is understood a solution of lemon oil in strong alcohol. In order to contain as much lemon oil as is supposed to be found in high-grade extracts the alcohol should constitute about 80 per cent of the sample. The alcohol is therefore the most valuable constituent of lemon extract, and manufacturers who turn out a low-grade product usually do so because of their economy of alcohol rather than of lemon oil. Owing to the fact that lemon extract is practically a saturated solution of oil of lemon in strong alcohol the sample may be examined by simple dilution with water. A teaspoonful of the oil in question may be placed in the bottom of an ordinary glass tumbler and two or three teaspoonfuls of water added. If the sample in question be real lemon extract the lemon oil should be thrown out of solution by reason of its insolubility in the alcohol after its dilution with water. The result is at first a marked turbidity, and later the separation of the oil of lemon on the top of the aqueous liquid. If the sample remains perfectly clear after the addition of water, or if a marked turbidity is not produced, it is a low grade product and contains very little, if any, oil of lemon.

Fruit Products.

Adulteration of fruit products is practically confined to jellies and jams. Contrary to the general belief, gelatin is never used in making fruit jelly. In the manufacture of the very cheapest grade of jellies starch is sometimes employed. Jellies containing starch, however, are so crude in their appearance that the most superficial inspection is sufficient to demonstrate that they are not pure fruit jellies. From their appearance no one would think it worth while to examine them to determine their purity.

Natural fruit jellies become liquid on being warmed. A spoonful dissolves readily in warm water, although considerable time is required with those that are especially firm. The small fruits contain practically no starch, as apples do, and the presence of starch in a jelly indicates that some apple juice has probably been used in its preparation. (As stated above, jelly that has been thickened by starch paste will not be mistaken for fruit jelly).

Detection of Starch.—Dissolve a teaspoonful of jelly in a half teacupful of hot water, heat to boiling, and add drop by drop, while stirring with a teaspoon, a solution of potassium permanganate until the solution is almost colourless. Then allow the solution to cool and test for starch with tincture of iodine (see *prox.*). Artificially coloured jellies are sometimes not decolorised by potassium permanganate. Even without decolorising, however, the blue colour can usually be seen.

Detection of Glucose.—For the detection of glucose, a teaspoonful of the jelly may be dissolved in a glass tumbler or bottle in two or three tablespoonfuls of water. The vessel in which the jelly is dissolved may be placed in hot water if necessary to hasten the solution. In case a jam or marmalade is being examined, the mixture is filtered to separate the insoluble matter. The solution is allowed to cool, and an equal volume or a little more of strong alcohol

is added. If the sample is a pure fruit product the addition of alcohol causes no precipitation, except that a very slight amount of proteid bodies is thrown down. If glucose has been employed in its manufacture, however, a dense white precipitate separates, and after a time settles to the bottom of the liquid.

Detection of Foreign Seeds.—In addition to the forms of adulteration to which jellies are subject, jams are sometimes manufactured from the exhausted fruit pulp left after removing the juice for making jelly. When this is done residues from different fruits are sometimes mixed. Exhausted raspberry or blackberry pulp may be used in making "strawberry" jam, and *vice versa*. Some instances are reported of various small seeds, such as timothy, clover, and alfalfa seed, having been used with jams made from seedless pulp.

With the aid of a small magnifying glass such forms of adulteration may be detected, the observer familiarising himself with the seeds of the ordinary fruits.

Detection of Preservatives and Colours.—With jellies and jams salicylic and benzoic acids are sometimes employed. They may be detected by the methods already given.

Artificial colours, usually coal-tar derivatives, are sometimes used and may be detected as described under "Determination of Artificial Colours."

Meat Products.

As in many other classes of foods, certain questions important in the judgment of meats require practical experience and close observation rather than chemical training. This is especially true of meat products. The general appearance of the meat must largely guide the purchaser. If, however, the meat has been treated with preservatives and colouring matter its appearance is so changed as to deceive him. The preservatives employed with meat products are boric acid, borax, and sulphites. The methods for the detection of sulphites are not suitable for household use.

Detection of Boric Acid and Borax.—To detect boric acid (if its sodium salt, borax, has been used the same reaction will be obtained) about a tablespoonful of the chopped meat is thoroughly macerated with a little hot water, pressed through a bag, and two or three tablespoonfuls of the liquid placed in a sauce dish with fifteen or twenty drops of strong hydrochloric acid for each tablespoonful. The liquid is then filtered through filter-paper, and a piece of turmeric paper dipped into it and dried near a lamp or stove. If boric acid or borax were used for preserving the sample the turmeric paper should be changed to a bright cherry-red colour. If too much hydrochloric acid has been employed a dirty brownish red colour is obtained, which interferes with the colour due to the presence of boric acid. When a drop of household ammonia is added to the coloured turmeric paper, it is turned a dark green, almost black colour, if boric acid is present. If the reddish colour, however, was caused by the use of too much hydrochloric acid this green colour does not form.

(Caution.—The corrosive nature of hydrochloric acid must not be forgotten. It must not be allowed to touch the flesh, clothes, or any metal).

Detection of Colours.—The detection of colouring matter in sausage is often a difficult matter without the use of a compound microscope. It may sometimes be separated, however, by macerating the meat with a mixture of equal parts of glycerin and water to which a few drops of acetic or hydrochloric acid have been added. After macerating for some time the mixture is filtered, and the colouring matter detected by means of dyeing wool in the liquid thus obtained (see p. 248).

Spices.

Although ground spices are very frequently adulterated, there are few methods that may be used by one who has not had chemical training, and who is not skilled in the

use of a compound microscope, for the detection of the adulterants employed. The majority of the substances used for the adulteration of spices are of a starchy character. Unfortunately for our purposes, most of the common spices also contain a considerable amount of starch. Cloves, mustard, and cayenne, however, are practically free from starch, and the presence of starch in the ground article is proof of adulteration.

Detection of Starch in Cloves, Mustard, and Cayenne.—A half teaspoonful of the spice in question is stirred into half a cupful of boiling water, and the boiling continued for two or three minutes. The mixture is then cooled. If of a dark colour, it is diluted with a sufficient amount of water to reduce the colour to such an extent that the reaction formed by starch and iodine may be clearly apparent if starch be present. The amount of dilution can only be determined by practice, but usually the liquid must be diluted with an equal volume of water, or only one-fourth of a teaspoonful of the sample may be employed originally. A single drop of tincture of iodine is now added. If starch is present, a deep blue colour, which in the presence of a large amount of starch appears black, is formed. If no blue colour appears, the addition of the iodine tincture should be continued, drop by drop, until the liquid shows by its colour the presence of iodine in solution.

Detection of Colours.—Spice substitutes are sometimes coloured with coal-tar colours. These products may be detected by the methods given (see p. 248).

Vinegar.

A person thoroughly familiar with vinegar can tell much regarding the source of the article from its appearance, colour, odour, and taste.

If a glass be rinsed out with the sample of vinegar and allowed to stand for a number of hours or overnight, the odour of the residue remaining in the glass is quite different with different kinds of vinegar. Thus, wine vinegar has the odour characteristic of wine, and cider vinegar has a peculiar fruity odour. A small amount of practice with this test enables one to distinguish with a high degree of accuracy between wine and cider vinegars and the ordinary substitutes.

If a sample of vinegar be placed in a shallow dish on a warm stove or boiling tea-kettle and heated to a temperature sufficient for evaporation and not sufficient to burn the residue, the odour of the warm residue is also characteristic of the different kinds of vinegar. Thus, the residue from cider vinegar has the odour of baked apples, and the flavour is acid and somewhat astringent in taste, and that from wine vinegar is equally characteristic. The residue obtained by evaporating vinegar made from sugar-house products and from spirit and wood vinegar coloured by means of caramel has the peculiar bitter taste characteristic of caramel.

If the residue be heated until it begins to burn, the odour of the burning product also varies with different kinds of vinegar. Thus, the residue from cider vinegar has the odour of scorched apples, while that of vinegars made from sugar-house wastes and of distilled and wood vinegars coloured with a large amount of caramel has the odour of burnt sugar. In noting these characteristics, however, it must be borne in mind that, in order to make them conform to these tests, distilled and wood vinegars often receive the addition of apple jelly.

As stated above, the cheaper forms of vinegar, especially distilled and wood vinegar, are commonly coloured with caramel, which can be detected by the method given (see p. 249).

Literary Intelligence.—Messrs. Harper and Brothers are adding, within the next few days, a new volume to their "Library of Living Thought." It is by Sir William Crookes, who writes on "Diamonds" and gives the result of his research in the laboratory, on the South African diamond fields, and among the meteorites of Arizona.

A REVISION OF THE ATOMIC WEIGHTS OF IODINE AND SILVER.*

(PRELIMINARY PAPER).

By GREGORY PAUL BAXTER and GEO. STEPHEN TILLEY.

(Continued from p. 261).

The Determination of Iodine in Iodine Pentoxide.—The analysis of the iodine pentoxide for iodine was effected by dissolving the substance in water, reducing the iodic acid solution to hydriodic acid with a suitable reducing agent, and titrating the hydriodic acid against a weighed amount of silver.

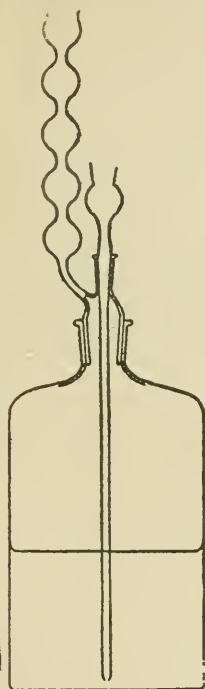
The operation in detail was as follows:—After being weighed, the boat with its contents was placed in a large thick-walled flask, and immediately covered with about 500 cc. of the purest water, in which it slowly dissolved. Even when the pentoxide was slightly coloured the solution was colourless to the eye and absolutely clear. The weighing-bottle was rinsed with water, and the rinsings were added to the main solution in the flask. In a number of early experiments the reduction was accomplished by slowly pouring the dilute solution of iodic acid into a solution of a slight excess of sulphurous acid. Very nearly the theoretical amount of the purest silver was weighed out and dissolved in re-distilled nitric acid diluted with an equal volume of water, in a flask provided with a column of bulbs to collect possible splatterings during the solution of the silver. As a matter of fact, the silver was caused to dissolve so slowly that only a very small quantity of gas was evolved. After the silver was completely dissolved, the solution was diluted with an equal volume of water, and heated until free from nitrous acid. This latter precaution was especially necessary, since nitrous acid readily liberates iodine from iodides, while nitric acid has this effect only when hot or rather concentrated. Finally, the solution was diluted until at least as dilute as thirtieth normal, and was added with constant agitation to the solution of the hydriodic acid which had been diluted to a similar concentration in a large glass-stoppered precipitating bottle. The whole was then thoroughly shaken, and allowed to stand until clear. In order to determine whether silver or iodide was in excess, 30 cc. portions of the solution were tested with silver nitrate and hydriodic acid in the nephelometer. The results of these earlier analyses were extremely unsatisfactory, the end-point changing continuously with time, and an unreasonably large amount of silver was required. This could not have been due to occlusion of silver nitrate by the silver iodide, since it has already been shown by one of us that at concentrations less than thirtieth normal the latter difficulty is too small to have an appreciable effect (Baxter, *Proc. Am. Acad.*, 1905, xli., 77). The cause of the trouble was finally traced to occlusion of silver sulphate by the silver iodide. Richards and Jones (*Pub. Carnegie Institution*, 1907, lxix., 73) found that silver chloride occludes silver sulphate very markedly and tenaciously, hence it is not in the least surprising to find the same difficulty here. It is to be noted that the concentration of sulphuric acid in these experiments is relatively large, *three molecules* of sulphuric acid being produced in the reduction for every *atom* of iodine. That this difficulty did not appear in the above mentioned researches upon the ratio of iodine to silver, where iodine was reduced with sulphurous acid and the hydriodic acid titrated against silver, is undoubtedly due to the fact that the concentration of sulphuric acid was relatively much lower, only *one molecule* of sulphuric acid being formed in the reduction of one *molecule* of iodine.

A search for a more satisfactory reducing agent than sulphurous acid failed to reveal any substance more promising than hydrazine, for the reduction of iodic acid with this substance yields only hydriodic acid, nitrogen, and water. (Brown and Shetterly have shown that no

* Contribution from the Chemical Laboratory of Harvard College From the *Journal of the American Chemical Society*, xxxi., No. 2.

hydronitric acid is formed by the action of hydrazine on iodates or iodine, *Journ. Am. Chem. Soc.*, 1908, xxx., 53). In order to avoid the introduction of undesirable acids, the hydrazine was used in the form of a solution of the hydroxide instead of as a salt. The hydrazine hydroxide was made by distilling either the chloride or the sulphate with a concentrated solution of a considerable excess of sodium hydroxide in a platinum still. The product was then re-distilled in the platinum still to eliminate possible traces of chlorides, and was preserved in a platinum flask. Even when made from the chloride, the doubly distilled product was absolutely free from chlorides. The approximate concentration of the solution was determined shortly before use by titration against a standard solution of iodic acid or potassium permanganate. Preliminary experiments showed that there is no danger of the reduction of the silver salts by a slight excess of hydrazine in nitric acid solution.

Special pains were taken in the reduction of the iodic acid with hydrazine to avoid any possibility of loss of iodine by volatilisation. The solution of the iodic acid was transferred to an 8-litre bottle with a carefully ground



APPARATUS FOR REDUCTION OF IODIC ACID.

stopper, and, after the iodic acid had been neutralised with ammonia, very slightly less than the theoretical quantity of hydrazine hydroxide was added. Since in alkaline solution hydrazine is without effect upon iodic acid, the solution was next made acid by slow addition of nitric acid.

As soon as hydriodic acid has begun to be formed, iodine is freed by interaction of the hydriodic acid with the iodic acid. Lest any of this iodine be volatilised from the solution before it could be reduced by the hydrazine, the nitric acid was introduced at the bottom of the solution through a long funnel. Thus iodine was sure to be completely reduced before reaching the surface of the solution. A specially devised stopper shown in the accompanying diagram provided for the escape of the nitrogen through a long column of bulbs, which served to catch splatterings or soluble vapours, if any reached this point. As a further precaution against the escape of iodine a small quantity

of sulphurous acid was poured into the bottle through the train of bulbs. This sulphurous acid served also to complete the reduction of the iodic acid. The amount of sulphuric acid formed in this way was not sufficient, however, to produce appreciable occlusion of silver sulphate.

After the reduction and subsequent dilution of the solution to a concentration between thirtieth and fiftieth normal, the hydriodic acid was precipitated with a dilute solution of a weighed amount of silver as before described. On account of the large bulk of the mother-liquor, 6 to 7 litres, the end-point as determined in the nephelometer was somewhat uncertain, especially since it seemed to be complicated by a minute trace of silver iodide held in suspension. Hence, instead of attempting to use exactly the theoretical quantity of silver, an amount was employed a few tenths of a mgrm. in excess of the required quantity. Then this excess was determined by evaporating the supernatant liquid to a very small bulk, precipitating the excess of silver as silver iodide, and determining the silver iodide either gravimetrically upon a Gooch-Munroe-Neubauer crucible, or nephelometrically by comparison with dilute standard solutions of silver. Before evaporation, the supernatant solution was carefully filtered through the Neubauer crucible, and the precipitate of silver iodide was washed by decantation several times with pure water to remove any adsorbed silver nitrate. That washing was able to remove any adsorbed silver nitrate was shown by treating a very carefully washed precipitate of silver iodide resulting from one of the analyses with a solution of silver containing a few tenths of a mgrm. of silver in 6 litres. After thorough agitation with the precipitate the solution was filtered and evaporated as in the analyses, after washing of the precipitate. Practically all this silver was found in the evaporated solution. Although the silver determined in this way includes the silver iodide dissolved in the mother-liquor, the error introduced is very small, the solubility of silver iodide being probably at least as low as 0.0000035 gm. per litre (Kohlrausch, *Zeit. Phys. Chem.*, 1904, l., 355). The platinum boat was not appreciably changed in weight.

The Determination of Moisture in Iodine Pentoxide.—The determination of the water content of the iodine pentoxide, when dried under the conditions used in the analyses for iodine, was fully as difficult as the iodine determination, and it was in preliminary attempts to determine the water content that evidence was obtained which led to the adoption of the above precautions for reducing the water content to a constant low value. The method of operation consisted, in brief, in completely decomposing the pentoxide into iodine and oxygen by heating in a current of dry air, and, after removing the iodine as far as possible by condensation, and finally by a layer of hot silver, collecting the water in a weighed phosphorus pentoxide tube. Great pains were taken that the iodine pentoxide should be prepared for the water determinations exactly as for iodine determinations. In order to avoid absorption of water between the heating and the decomposition, the decomposition of the pentoxide took place immediately upon the completion of the heating without interruption of the experiment, the weighing of the pentoxide, which need not be very accurate on account of the low per cent of water, having taken place before the long heating at 240°.

The iodic acid used in the water determinations was not made from either purified iodine or purified nitric acid, and most of it was prepared in glass vessels. However, it was very carefully purified by repeated crystallisation from aqueous solution in platinum vessels with centrifugal drainage of the crystals in each case, and gave every outward evidence of great purity. Not only were the final crystals pure white, but the final mother-liquor was colourless. The crystals gave a perfectly clear solution in water, and left no appreciable residue when decomposed in the platinum boat.

The platinum boat, containing about 25 grms. of acid which had been inoculated with the second phase, was

freed from water by heating at 100° and then at $220^{\circ} +$ in the usual way. It was then bottled and weighed. Next, the boat was transferred to a long hard glass tube very carefully ground into the socket of the bottling apparatus, and was heated to 240° for four hours in a current of dry air. Toward the end of the heating all of the apparatus beyond the phosphorus pentoxide drying tube was gently heated with a Bunsen flame in order to dislodge any adsorbed water from the inside surface of the glass. Although by far the greater part of the iodine formed in the decomposition condensed in the hard glass tube, a small quantity of iodine vapour was always carried along by the current of gases (Baxter, Hickey, and Holmes, "The Vapour Pressure of Iodine," *Journ. Am. Chem. Soc.*, 1907, xxix., 127). For the absorption of this iodine vapour a small hard glass tube containing small electrolytic crystals of silver which had been dried by heating to about 400° in a vacuum, was carefully ground on the end of the hard glass tube. This tube was attached to the hard glass tube during the decomposition of the pentoxide, and was heated to very dull redness. The column of metallic silver was several inches in length, and although considerable silver iodide was produced at the end of the column nearest the decomposition tube, the silver at the other end of the column remained perfectly bright through all the determinations, showing the absorption of iodine to have been complete.

The U-tubes for the absorption of water were provided with glass stopcocks, and were filled with phosphorus pentoxide which had been freshly sublimed in a current of oxygen. They were weighed by substitution, with the use of a similar tube as counterpoise. Before being weighed, the tubes were wiped with a damp cloth, and were allowed to stand near the balance case for at least an hour. The tubes were weighed with one stopcock open. The balance was provided with a few mgrms. of radium bromide of radio-activity 10,000 to dispel electrical charges. Under these conditions no difficulty was experienced in weighing the tubes within a few hundredths of a mgrm., since they quickly came to constancy in the balance case, and retained their weights unchanged for days at a time. Two phosphorus pentoxide tubes were used in the first experiments, but since the gain in weight of the second tube was found to be negligible in all cases where it was used, the second tube was omitted in the later experiments. Still another phosphorus pentoxide tube was placed beyond the weighed tubes as a protection against the back diffusion of moisture. Blank experiments were usually run after the collection of the water resulting from the decomposition. Frequently no gain in weight of the tube in these blank experiments could be detected, and in no case did the gain in weight amount to more than one-tenth of a mgrm.

The decomposition of the iodine pentoxide was effected by removing the aluminium oven, and heating the tube to the temperature of decomposition of the pentoxide, about 350° , with a Bunsen burner. Decomposition was conducted as evenly as possible so as to avoid an unduly rapid current of oxygen from the apparatus with consequent incomplete absorption of the water. When decomposition was complete the condensed iodine was heated above its melting-point to set free traces of adsorbed moisture. Then the decomposition tube was swept out with a current of dry air, and the absorption tube was weighed. In four experiments carried out as above the following results were obtained:—

No. of analysis.	Weight of I_2O_5 , grms.	Weight of H_2O , grm.	Per cent of H_2O .
1.	25.0	0.00060	0.0024
2.	20.7	0.00032	0.0016
3.	26.1	0.00067	0.0026
4.	24.6	0.00060	0.0024

Average.. .. 0.0023

In addition, several experiments were performed in order to determine the effect of varying the conditions of treat-

ment. In Analysis 5 the heating at 240° lasted only one hour, and in Analysis 6 the iodine pentoxide was heated for four hours at 260° . In Analyses 7 to 11 only a very small quantity of the second phase was used to inoculate the pentoxide. In Analyses 7 and 8 the substance was powdered to the same degree of fineness as in the first set of experiments, in Analysis 9 the material was very finely powdered, and in Analyses 10 and 11 the material was rather coarsely powdered.

No. of analysis.	Weight of I_2O_5 , grms.	Weight of H_2O , grms.	Per cent of H_2O .
5.	25.5	0.00066	0.0026
6.	25.3	0.00062	0.0025
7.	24.9	0.00113	0.0045
8.	26.8	0.00100	0.0037
9.	18.9	0.00077	0.0041
10.	21.3	0.00133	0.0062
11.	25.0	0.00155	0.0062

The differences in the composition of the pentoxide actually observed, even with very widely differing methods of treatment, are so small that there can be no doubt that the slight variations in treatment likely to occur in the course of an analysis could not have had an appreciable effect.

(To be continued.)

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Anniversary Meeting, November 30th, 1908.

At the Anniversary Meeting of the Royal Society, held on Tuesday last, the following Council and Officers were elected for the ensuing year:—

President—Sir Archibald Geikie, K.C.B., D.C.L., Sc.D., LL.D.

Treasurer—Alfred Bray Kempe, M.A., D.C.L.

Secretaries—Prof. Sir Joseph Larmor, D.Sc., D.C.L., LL.D.; Prof. John Rose Bradford, M.D., D.Sc.

Foreign Secretary—Sir William Crookes, D.Sc., LL.D.

Other Members of Council—Herbert Brereton Baker, D.Sc.; Walter Holbrook Gaskell, M.D.; Prof. Ernest Howard Griffiths, Sc.D.; Prof. Horace Lamb, Sc.D.; Prof. Hector Munro Macdonald, M.A.; Major Percy Alexander MacMahon, Sc.D.; Charles James Martin, M.D.; Sir Andrew Noble, Bart., Sc.D.; Prof. William Henry Perkin, Ph.D.; Prof. Edward Bagnall Poulton, D.Sc.; Prof. John Henry Poynting, Sc.D.; Lieut.-Col. David Prain, C.I.E.; Prof. Ralph Allen Sampson, M.A.; Arthur Everett Shipley, M.A.; Rt. Hon. Sir James Stirling, M.A.; Aubrey Strahan, Sc.D.

The following medals were awarded:—

The Copley Medal to Dr. G. W. Hill, on the ground of his researches in Mathematical Astronomy.

A Royal Medal to Prof. A. E. H. Love, on the ground of his researches in the theory of Elasticity and cognate subjects.

A Royal Medal to Major Ronald Ross, on the ground of his researches in connection with Malaria.

The Davy Medal to Sir James Dewar, on the ground of his researches at Low Temperatures.

The Hughes Medal to Dr. R. T. Glazebrook, on the ground of his researches on Electrical Standards.

CHEMICAL SOCIETY.

Ordinary Meeting, November 18th, 1909.

Prof. HAROLD B. DIXON, F.R.S., President, in the Chair.

It was announced from the Chair that, on the motion of the PRESIDENT, seconded by Dr. HUGO MÜLLER, the Council of the Society had, that afternoon, unanimously passed the following resolution:—The Council of the

Chemical Society have heard with deep regret of the death of Dr. J. W. Russell, F.R.S., Past President of the Society. The Council recall the long services of Dr. Russell to the Society extending over nearly half a century. Elected a Fellow of this Society in 1851, Dr. Russell was first chosen a member of the Council in 1863, and with one short interval he served the Society continuously until his death. He was Vice-President in 1872, Secretary from 1873 to 1875, Treasurer from 1875 to 1889, and President from 1889 to 1891. Dr. Russell's communications to the Society began in the year 1855. Chemists throughout the world recognise the scientific importance of his memoirs on the atomic weights of Nickel and Cobalt, on the Absorption Spectra of Solutions, and on the action of metals and of wood on photographic plates; and all workers on gas analysis are indebted to Dr. Russell for the new methods and apparatus he designed for the manipulation and measurement of gases. On behalf of the Chemical Society the Council desire to express their sense of the great loss that the Society and British Science have sustained, and beg to convey to the relatives of Dr. Russell their sincerest sympathy.—Signed, on behalf of the Society,

HAROLD B. DIXON, President.

It was stated from the Chair that the Society had become indebted to Prof. Meldola, F.R.S., for an interesting photograph of the Paris Exhibition July, 1909.

Certificates were read for the first time in favour of Messrs. Arthur Jacques, B.Sc., 23, St. Oswin's Avenue, Cullercoats, Northumberland; Samuel Judd Lewis, B.Sc., Ph.D., 122, Newington Causeway, S.E.; Herbert William Southgate, B.Sc., 130, Horseferry Road, Westminster, S.W.; Stuart Jardine Norris Wolfenden, The Grange, Sidcup, Kent.

Certificates have been authorised by the Council for presentation to ballot under By-law 1. (3) in favour of Messrs. Edmund Victor Flack, Mayville, Wigtown Road, Green Point, S. Africa; John Muller, B.A., Government Analytical Laboratory, Grahamstown, Cape Colony; Joas Cornelio Rodrigues Peixoto, 52, Rua N.S. Copacabana, Rio de Janeiro (Brazil); Charles Tapp, Cradock, Cape of Good Hope; Joseph Pretty Wright, 883, Burrard Street, Vancouver, B.C.

The Council has ordered the following letter and report to be printed in the *Journal* and *Proceedings* of the Society:

Imperial College of Science and Technology,
South Kensington, London, S.W.,
November 17th, 1909.

GENTLEMEN,—I beg to present to the Council of the Chemical Society the Report of the International Committee on Atomic Weights, 1910, to which I have affixed, as desired by them, the signatures of Profs. Ostwald and Urbain.

Since the Committee last reported, new determinations have been made of the atomic weights of chlorine, nitrogen, carbon, iodine, silver, phosphorus, arsenic, chromium, tellurium, mercury, palladium, krypton, and xenon.

Certain of the numbers obtained, if confirmed, would necessitate minor alterations in the tables, but as additional determinations are promised we prefer to make no very great changes until corroborative evidence is forthcoming. We suggest, however, that the value of Cr should be 52.0; that of As should be changed to 74.96; and we adopt the new values for krypton and xenon.—I am, Gentlemen, your obedient Servant,

T. E. THORPE.

The Hon. Secretaries, The Chemical Society,
Burlington House, London, W.

Report of the International Committee of Atomic Weights, 1910.

Since the preparation of our last report there has been much activity in the determination of atomic weights. A brief summary of the results obtained is as follows:—

Chlorine.—A novel comparison of chlorine with oxygen is due to Guye and Fluss (*Journ. Chim. Phys.*, 1908, vi., 732). Nitrosyl chloride, NOCl, was first weighed, and

then distilled over silver to absorb chlorine, then over heated copper to absorb oxygen, and finally over metallic calcium, which retained the nitrogen. The complete analysis of the chloride was thus effected. From the direct weights of the oxygen and chlorine, Cl = 35.468.

Nitrogen.—In the investigation just cited, Guye and Fluss give data which correspond to N = 14.006. Guye and Pintza (*Comptes Rendus*, 1908, cxlvii., 925) determined the density of the mixed gases produced by the decomposition of ammonia, and so measured its composition by volume. If H = 1.0076, then N = 14.014. The authors regard the determination as having only a significance corroborative of the lower value for nitrogen.

The ratio AgCl : NH₄Cl : 100 : 37.3217 has been measured by Richards, Koethner, and Tiede (*Journ. Am. Chem. Soc.*, 1909, xxxi., 6). Reduced with Ag = 107.881, Cl = 35.4574, and H = 1.0076, N = 14.0085. If H = 1.0078, N = 14.008. The values assigned to silver and chlorine are derived from former researches by Richards and his colleagues in the Harvard laboratory.

Carbon.—From the ratio between silver and tetraethylammonium bromide, as measured by Scott (*Trans.*, 1909, xcv., 1200), C = 12.017 when Ag = 107.88. A single experiment with the corresponding methyl compound gave C = 12.019. These values are too high to be accepted until they have been confirmed by other methods.

From the density of methane, Baume and Perrot (*Comptes Rendus*, 1909, cxlviii., 39) find C = 12.004. From the density of toluene, as determined by Ramsay and Steele, Leduc (*Comptes Rendus*, 1909, cxlviii., 832) computes C = 12.003.

Iodine and Silver.—Baxter and Tilley (*Journ. Am. Chem. Soc.*, 1909, xxxi., 201) have determined the ratio between iodine pentoxide and silver. The pentoxide was reduced by means of hydrazine, and the hydriodic acid so produced was balanced in the usual way against silver. From the ratio thus found, I₂O₅ : 2Ag : 100 : 64.6225 and 64.6230 (two series), combined with the ratio I : Ag : 100 : 84.8843, the authors find that the atomic weight of Ag lies between 107.847 and 107.850. The corresponding value for iodine is I = 126.891.

Phosphorus.—From the density of phosphine, PH₃, Ter Gazarian (*Comptes Rendus*, 1909, cxlviii., 1397) finds P = 30.906.

Arsenic.—Atomic weight re-determined by Baxter and Coffin (*Journ. Am. Chem. Soc.*, 1909, xxxi., 297). The ratios Ag₃AsO₄ : 3AgCl and Ag₃AsO₄ : 3AgBr were determined by two methods, one by solution and precipitation in the usual way, the other by heating the arsenate in a stream of hydrochloric or hydrobromic acid. The final mean result is As = 74.957 when Ag = 107.880.

Chromium.—From analyses of silver chromate by two methods, Baxter, Mueller, and Hines (*Journ. Am. Chem. Soc.*, 1909, xxxi., 529) find Cr = 52.008 when Ag = 107.88. With similar analyses of silver dichromate, Baxter and Jesse (*Journ. Am. Chem. Soc.*, 1909, xxxi., 541) find Cr = 52.013. The mean value is 52.01.

Tellurium.—Lenher (*Journ. Am. Chem. Soc.*, 1909, xxxi., 20) converted the double bromide K₂TeBr₆ into 2KCl by heating, first in a stream of chlorine, and afterwards in hydrochloric acid. Sixteen very concordant experiments were made, giving the molecular ratio between the two compounds. The final mean value is Te = 127.55.

Mercury.—Analyses of mercuric chloride have been made by Easley, who determined the proportion of mercury in the compound, and also the ratio HgCl₂ : 2AgCl (private communication; Easley's work is soon to be published). By the first method, Hg = 200.48; by the second method, Hg = 200.62. These values are surprisingly high; but as Easley is to continue his investigation, it would be unwise to accept them until his work is all done. It is quite possible that the increase may be ultimately verified.

Palladium.—Atomic weight determined by Gutbier, Haas, and Gebhardt by analyses of palladosamine bromide (*Journ. Prakt. Chem.*, 1909, [ii.], lxxix., 457; this includes the work of Haas, cited in the Report for 1909). The final

International Atomic Weights. (1910).
(O = 16).

Aluminium	Al	27.1
Antimony	Sb	120.2
Argon	A	39.9
Arsenic	As	74.96
Barium	Ba	137.37
Bismuth	Bi	208.0
Boron	B	11.0
Bromine	Br	79.92
Cadmium	Cd	112.40
Cæsium	Cs	132.81
Calcium	Ca	40.09
Carbon	C	12.00
Cerium	Ce	140.25
Chlorine	Cl	35.46
Chromium	Cr	52.0
Cobalt	Co	58.97
Columbium	Cb	93.5
Copper	Cu	64.57
Dysprosium	Dy	162.5
Erbium	Er	167.4
Europium	Eu	152.0
Fluorine	F	19.0
Gadolinium	Gd	157.3
Gallium	Ga	69.9
Germanium	Ge	72.5
Glucinum	Gl	9.1
Gold	Au	197.2
Helium	He	4.0
Hydrogen	H	1.008
Indium	In	114.8
Iodine	I	126.92
Iridium	Ir	193.1
Iron	Fe	55.85
Krypton	Kr	83.0
Lanthanum	La	139.0
Lead	Pb	207.10
Lithium	Li	7.0
Lutecium	Lu	174.0
Magnesium	Mg	24.32
Manganese	Mn	54.93
Mercury	Hg	200.0
Molybdenum	Mo	96.0
Neodymium	Nd	144.3
Neon	Ne	20.0
Nickel	Ni	58.68
Nitrogen	N	14.01
Osmium	Os	190.0
Oxygen	O	16.00
Palladium	Pd	106.7
Phosphorus	P	31.0
Platinum	Pt	195.0
Potassium	K	39.10
Praseodymium	Pr	140.6
Radium	Ra	226.4
Rhodium	Rh	105.9
Rubidium	Rb	85.45
Ruthenium	Ru	101.7
Samarium	Sa	150.4
Scandium	Sc	44.1
Selenium	Se	79.2
Silicon	Si	28.3
Silver	Ag	107.88
Sodium	Na	23.00
Strontium	Sr	87.62
Sulphur	S	32.07
Tantalum	Ta	181.0
Tellurium	Te	127.5
Terbium	Tb	159.2
Thallium	Tl	204.0
Thorium	Th	232.42
Thulium	Tm	168.5
Tin	Sn	119.0
Titanium	Ti	48.1
Tungsten	W	184.0

Uranium	U	238.5
Vanadium	V	51.2
Xenon	Xe	130.7
Ytterbium (Neoytterbium)	Yb	172.0
Yttrium	Y	89.0
Zinc	Zn	65.37
Zirconium	Zr	90.6

most probable mean value when $N_2H_6Br_2 = 193.908$ is $Pd = 106.689$.

Krypton and Xenon.—Moore (*Trans.*, 1908, xciii., 2181) isolated krypton and xenon in considerable quantities from the residues from 120 tons of liquid air. Calculated from the densities of the two gases, the atomic weights are $Kr = 83.012$ and $Xe = 130.70$.

It will be seen from the evidence given above that few changes are needed in the table of atomic weights. Chromium, 52.01, may be rounded off to 52, as compared with the 52.1 formerly accepted. Arsenic becomes 74.96, in accordance with the work of Baxter and Coffin. The new values for krypton and xenon should also be adopted. As regards mercury, action may be deferred until more evidence is received.

F. W. CLARKE.
W. OSTWALD.
T. E. THORPE.
G. URBAIN.

(To be continued).

NOTICES OF BOOKS.

Laboratory Notes on Iron and Steel Analyses. By WALTER MACFARLANE, F.I.C. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1909.

THE author of this book has a particularly wide knowledge of methods of analysing iron and steel, and has had experience both in directing operations in the laboratory attached to iron and steel works, and also of teaching the students of educational institutions the first principles of the processes. Hence he is well qualified to recommend practically useful methods and to write authoritatively concerning experimental details. He gives in this book an excellently arranged and full course of practical work in iron and steel analysis; in each experiment the outline of the method is first given, so that the student is quite clear as to what he is driving at before he proceeds to the consideration of the details. Full typical calculations are included, and many rules to shorten or simplify the working out of results are stated. The student is given no possible chance of making a mistake either in the choice of the dimensions of his apparatus or in carrying out the processes; in fact, perhaps attention to detail is carried to excess. For instance, in describing a gravimetric analysis there can surely be no need for telling the student to weigh and "note the weight," and if in the list of apparatus required in a titrimetric estimation a burette and burette stand are included, even the least imaginative student might be trusted to conclude that the burette was to be fixed in the stand, and explicit directions to that effect might be omitted. This excess of detail makes the book appear to contain much more matter than it really does, but, on the other hand, the use of the book in the laboratory would certainly lighten the task of the demonstrator and enable him to supervise the work of a larger number of students than if they had at hand less detailed instructions.

The Periodic Law. By A. E. GARRETT, B.Sc. (by research) Lond., F.R.A.S. London: Kegan Paul, Trench, Trübner, and Co., Ltd. 1909.

AT the present time possibly more interest is felt in the investigation of the reasons which underlie the Periodic System than in the facts summarised by the Law; hence

readers of this book will perhaps regret that more space was not devoted in it to the consideration of the structure of the atom which is discussed in the last chapter. The difficulty of making such a highly technical subject as the Periodic Law interesting to the general reader is apparent throughout the book, which, however, is in most parts not by any means difficult reading even for those who have very little knowledge of chemistry. Early attempts at classification are discussed in some detail, and claims to priority are carefully weighed, a very fair spirit being displayed towards all workers who appeared to be true fore-runners of De Chancourtois, Newlands, Mendeleeff, and Lothar Meyer. The book contains a great number of graphic representations, diagrams, and tables, which help to make the main facts clear.

London Matriculation Directory, September, 1909. London: The University Tutorial Press, Ltd.

The series of Matriculation Directories of which this volume is the fifty-third is well known to candidates for the examination in question, who have found the earlier volumes almost invaluable. In this number, which contains the papers set in the last examination (September, 1909) the usual advice on the choice of text-books is given, and also full solutions of many of the papers. The criticisms of each paper are intended to give the student some idea as to whether the papers are above the average standard of difficulty or whether he may expect rather less easy questions, and the student who is working alone will find that he can get great assistance from them and from the general advice given in the introduction.

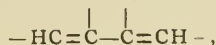
CORRESPONDENCE.

THIELE'S VALENCIES.

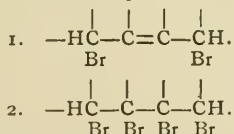
To the Editor of the Chemical News.

SIR,—May I crave the hospitality of your columns to put forward a suggestion with reference to the phenomenon known as Thiele's conjugated linkages.

If we have in a molecule the group—

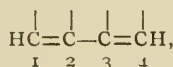


the addition of bromine takes place in two stages giving—



In order to explain this phenomenon we must ask ourselves the question—"Which two out of the above four carbon atoms is the more unsaturated?"

Let us number the carbon atoms:—



and confine our attention for a moment to the atoms 2 and 3. The fact that we represent the carbon atom 2 joined to carbon 1 by a double bond is usually taken to represent the fact that the total affinity of the carbon atoms is not saturated.

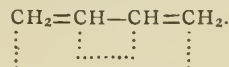
Now the whole phenomena of organic chemistry go to show that the free affinities of carbon atoms can mutually satisfy each other. Therefore the free affinity of the atom 2 would saturate that of the atom 3, whereas the free affinity of the atoms 1 and 4 are literally free, on account of the greater distance in space between these two

atoms. We therefore see that the atoms 1 and 4 are more unsaturated than the atoms 2 and 3.

It may be pointed out that this difference in saturation need be only a small quantity in order to predestine the course of the reaction in the way it does.

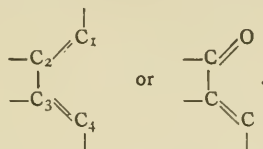
The above explanation is, I think, similar in principle to the fundamental idea underlying Thiele's account of the phenomenon. I wish to propose in this letter an alternative mode of representing this idea in our formulæ.

In order to explain these phenomena Thiele assumed the existence in these compounds of a new kind of valency known as partial valency. The group is written thus—

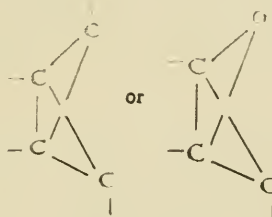


The dotted lines represent the partial valencies. The disadvantages of this method are that it seems to represent carbon in these compounds as possessing a valency greater than 4, and that it assumes a special kind of valency in order to account for a few isolated phenomena in organic chemistry.

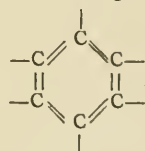
If we write the carbon atoms more according to their relative positions in space—



If the double bonds attract each other we have—



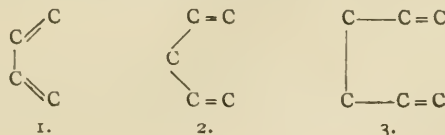
It is obvious from this formula that the atoms 1 and 4 are more open to attack than 2 and 3. If we apply these views to benzene instead of taking Thiele's formula—

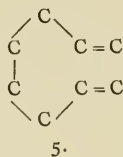
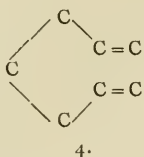


we obtain the familiar formula—



By means of these views we arrive at the following deduction. If we take the series—

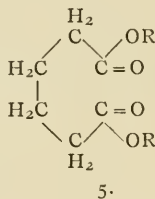
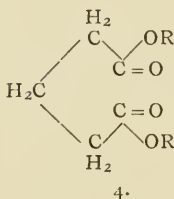
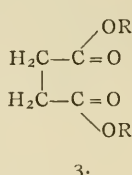
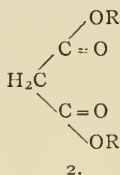
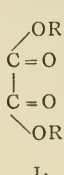




we would expect that the optical and chemical anomalies which are present in the group 1 would reappear higher up the series when we come to the groups 4 and 5.

This deduction has, in fact, been beautifully illustrated by some recent work by Hilditch (*Trans. Chem. Soc.*, October, 1909). This author has shown that optically

active compounds possessing the group $\text{C}=\text{C}-\text{C}=\text{C}$ possess abnormally high rotary power. On examining the rotary power of the menthyl and brucine esters of the series of acids from oxalic to sebacic acids—



it was found that the greatest anomaly existed in 1. The rotary power was then normal until we come to 5 (adipic acid), which shows quite a considerable anomaly. The anomaly is, of course, not so great as when the critical carbon atoms are actually contiguous.

Other experiments will be undertaken to prove this point.—I am, &c.,

A. WECHSLER.

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CHEMICAL NOTICES FROM FOREIGN SOURCES.

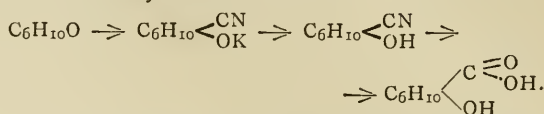
Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlix., No. 15, October 11, 1909.

Spectrographic Analysis of Blends.—G. Urbain.—When the arc spectra of various blends were studied it was found that out of 64 specimens, 38 contained germanium and 41 indium. The blends which were rich in germanium were generally rich in gallium and poor in indium. Nearly all the blends contained gallium, and all of them cadmium and lead. Iron and manganese were frequently present.

Derivatives of Hexahydro-oxybenzoic Acid.—P. J. Tarbouriech.—Hexahydro-oxybenzoic acid can be prepared by allowing potassium cyanide to act on cyclohexanone, decomposing the potassium compound thus formed by

dilute hydrochloric acid, and hydrating the nitrile with concentrated hydrochloric acid—



The author has prepared the potassium salt, the methyl, ethyl, and isoamyl esters and the amide of the acid. The methyl ester gives with methyl magnesium iodide a bitertiary glycol.

New Series of Leucobases and of Colouring Matters derived from Diphenylethane.—P. Lemout.—The alkyl derivatives of *pp*-diamidodiphenylethane are leucobases, for when oxidised they give a well marked coloration, and the coloured liquids thus obtained are capable of dyeing substances, giving a whole series of shades. Their action can be tested very readily with cotton mordanted with tannin. It seems probable that these amido-alkyl derivatives of diphenylethane owe their leucobasic properties not to their decomposition products but to their own constitution, and that they form a new series of leucobases.

MISCELLANEOUS.

Institute of Chemistry.—Of four candidates who presented themselves for Examination in Biological Chemistry, Bacteriology, Fermentation, and Enzyme Action, held from October 18th to 22nd, three passed. William John Read, B.Sc. (Manchester), has been elected to the Associateship of the Institute; and the following have been granted the Special Certificate in these subjects:—Robert Westrup Blair, F.I.C. (Laboratory of the Metropolitan Water Board); and Albert Edward Parkes, F.I.C. (Laboratory of the Public Analyst for the Borough of Stepney). The Examiner in Biological Chemistry was Dr. A. Harden, F.R.S., F.I.C., and the Examiners in General Chemistry were Mr. Bertram Blount, F.I.C., and Prof. Herbert Jackson, F.I.C.

Allen's "Commercial Organic Analysis."—Messrs. J. and A. Churchill have a new edition of Vol. I. just ready for publication. This volume has been re-written under the editorship of Dr. H. Leffman and Mr. W. A. Davis, B.Sc. The subjects and authors are as follows:—Introduction, by W. A. Davis; Alcohols, by G. C. Jones, Malt and Malt Liquors, by Julian L. Baker; Wines and Potable Spirits, by G. C. Jones; Yeast, by Emil Schlichting; Neutral Alcoholic Derivatives, by Henry Leffmann; Sugars, by E. Frankland Armstrong; Starch and Isomers, by E. F. Armstrong; Paper and Paper-making Materials, by R. W. Sindall; Acid Derivatives of Alcohols, by Henry Leffmann. It will be seen that each subject is handled by an expert in his department.

NOTES AND QUERIES.

. Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Charred Leather Powder.—A correspondent wishes to know the address of the maker of charred leather powder for case hardening iron and steel, in this country or elsewhere.

MEETINGS FOR THE WEEK.

MONDAY, 6th.—Royal Society of Arts, 8. (Cantor Lectures). "Aeronautics," by C. C. Turner.
— Royal Institution, 5. (General Monthly Meeting).
— Society of Chemical Industry, 8. "Artificial Silk Industry," by W. P. Dreaper.
WEDNESDAY, 8th.—Royal Society of Arts, 8. "Destruction of Plumage Birds," by J. Buckland.
THURSDAY, 9th.—Royal Society of Arts, 4.30. "The Punjab," by Sir James Wilson, K.C.S.I.

VOL C., No. 2611.

By F. H. LORING.

3. The curves carry, or tend to carry, a regular recurring number of elements. The first and last curve of the first group take six elements each, and the intermediate ones three each with, at present, one or two exceptions. The second group harmonises with the first, except that the curves take, or tend to take, one more element each. The third group is not yet established, but it may be assumed that it would take all the remaining elements, the total number being estimated at about 106. These regularities are best shown by a table.

When the known elements are assigned to their places in the series, according to the above method, it will be seen that about the same number fall above zero (41) as below it (37), and that there are numerous gaps which divide them into groups characterised thus:—

$abc, defg, hij, \&c.,$ or $\begin{array}{ccc} & g & \\ c & f & i \\ b & e & j \\ a & d & h \end{array}, \&c.$

It will be observed that the number of elements, especially those of the central part of the table, are remarkably well balanced, and that there would be by extrapolation twenty-seven groups or single rows, and nine triple balanced groups (three rows each). The recurrence of nines is extraordinary, but presumably is, in itself, of no significance. It is perhaps of interest to note that the twin elements are fairly well-balanced. I—Te, for instance, is balanced by Pd—Ag in the same curious way that the number of elements in the outer rows of each triple group are equal. The lines joining the figures indicate the system of balances. The relations can hardly be coincidences, since there is not a single exception to mar the accuracy of the plan where the elements, whose weights are accurately known, are located, and where no more elements appear likely to be added. For example, an element having a weight of three would upset one of the balances.

Considerable interest appears to be centred round the inactive gases at the present time, since those elements, distinguished by being strongly radio-active, give off, under conditions of apparent atomic disintegration, inactive gases. There is still much uncertainty about these



SYMBOL	ELEMENTS. ATOMIC WTS	SYMBOL	ELEMENTS. ATOMIC WTS
Sc	SATELLITE(?) 0.27	Xe	XENON 130.7
H	HYDROGEN 1.007+	Cs	CESIUM 132.81
He	HELIUM 3.98(4)	Ba	BARIUM 137.37
Li	LITHIUM 7.00	La	LANTHANUM 139.0
Be	BERYLLIUM 9.1	Ce	CERIUM 140.25
Nb	— (?) 9.75	Pr	PRASEODYMIUM 140.6
B	BORON 11.0	Nd	NEODYMIUM 144.3
C	CARBON 12.00+	Sa	SAMARIUM 150.4
O	OXYGEN 16.000	Eu	EUROPIUM 152.0(?)
F	FLUORINE 19.0	Gd	GADOLINIUM 157.3
Ne	NEON 20.0	Tb	TERBIUM 159.2
Na	SODIUM 23.00	Dy	DYSPROSIUM 162.5
Mg	MAGNESIUM 24.32	Ho	HOLMIUM
Al	ALUMINIUM 27.1	Er	ERBIUM 167. (?)
Si	SILICON 28.3	Tu	THULIUM 168.5
P	PHOSPHORUS 31.0	Ny	NEOYTTERBIUM 172. (?)
S	SULPHUR 32.07	Lu	LUTECIUM 174. (?)
Cl	CHLORINE 35.46	RaEm	RADIUM EMANATION 175.
K	POTASSIUM 39.10		
Ar	ARGON 39.9		
Ca	CALCIUM 40.09		
Sc	SCANDIUM 44.1		
Ti	TITANIUM 48.1	Ta	TANTALUM 181.0
V	VANADIUM 51.2	W	TUNGSTEN 184.0
Cr	CHROMIUM 52.01		
Mn	MANGANESE 54.93	Os	OSMIUM 190.9
Fe	IRON 55.85	Ir	IRIDIUM 193.1
Ni	NICKEL 58.68	Pt	PLATINUM 195.0
Co	COBALT 58.97	Au	GOLD 197.2
Cu	COPPER 63.57	Hg	MERCURY 200.0
Zn	ZINC 65.37	Tl	THALLIUM 204.0
Ga	GALLIUM 70. (?)	Pb	LEAD 207.1
Ge	GERMANIUM 72.5	Bi	BISMUTH 208.0
As	ARSENIC 74.96		
Se	SELENIUM 79.2		
Br	BROMINE 79.92	Z' (?)	216.
Kr	KRYPTON 83.0		
Rb	RUBIDIUM 85.45	Ra	RADIUM 226.
Sr	STRONTIUM 87.62		
Yt	YTTRIUM 89.0	Th	THORIUM 232.4
Zr	ZIRCONIUM 90.6		
Nb	NIOBIUM 93.5	U	URANIUM 238.5
Mo	MOLYBDENUM 96.0		
Np	NIPPONIUM 100. (?)		
Ru	RUTHENIUM 101.7		
Rh	RHODIUM 102.9		
Pd	PALLADIUM 106.7		
Ag	SILVER 107.88		
Cd	CADMIUM 112.40		
In	INDIUM 114.8		
Sn	TIN 119.0		
Sb	ANTIMONY 120.2		
I	IODINE 126.92	Z ² (?)	251.
Te	TELLURIUM 127.5		

NITROGEN (N) = 14.007. I.C. VALUE 1909.

TABLE II.

phenomena, but many of the remarkable changes, &c., are amply confirmed. This unexpected behaviour of the aforesaid elements paves the way for a bold speculation which one would not like to have hazarded a few years ago, namely, that nitrogen is built up of helium and two other nactive elements. This is not a mere invention, but is based upon the singular fact that nitrogen does not fit into the system. Moreover, I have published some confirmatory evidence of a mathematical nature (*loc. cit., ut infra*), neglecting for the moment the purely chemical agreements in support of the scheme, which I need not repeat here. One of the most striking evidences, however, is that the

In the Kr-Xe series, the newly-discovered element, "nipponium," atomic weight about 100, is included, which brings the number to 17. This appears at first as presenting no serious difficulty if iodine is regarded as carrying a satellite, but the weight of the iodine residue, obtained by deducting the weight of the satellite, is such that it would constitute an element not to be found elsewhere in the table, and a further step is necessary to reduce the number of elements so as to give expression to the geometric regularity. I have previously shown that probably the weight of iodine is very close to 126.97 (126.965 or 126.963), and the weight of tellurium, 127.50, is regarded as fairly accurate, according to the latest determinations which were in themselves exceedingly concordant. However this may be, Te falls on a curve

TABLE III.

exactly, and the difference between its weight and that of iodine is of the order of 0.53 or 0.54, which is practically equal to two satellites. Therefore, iodine plus two satellites equals tellurium. Although this seems to get over the difficulty, it does not, on the other hand, accord with my first treatment, which arose partly from the position of iodine not being ideal with respect to bromine in the table prepared from the curves. This difficulty could be got over by assigning to iodine one satellite, as originally, and three to tellurium, in which case the latter element would fall exactly on curve No. 14, assuming the value of the satellite to be about 0.268. This would eliminate I or Te from the list and bring the total to 16. At any rate, whether nipponium is included or not, the iodine-tellurium difficulty does not necessarily weaken the proposed geometric law; rather it supports it, since the one element in excess of the theoretical number is decidedly out of place in the Periodic Table. One can hardly conceive that Nature "slipped a cog" when she made these twin elements, but probably the satellite is in some way responsible for the irregularity. Doubtless this phenomenon, if it may be so regarded, is similar to that here ascribed to nitrogen, and possibly a few other elements are thus compounded, as indeed one might judge from the "overcrowding" between xenon and the radium emanation. Regarding the satellite as virtually an impurity, it would appear to afford an explanation of the slight variations in weight of certain elements, most notably those of the rare earth class, without apparently a corresponding variety in chemical properties, as found in other parts of the table.

A Periodic Arrangement of the Elements by Displacements.

Approaching the subject from another direction, I may, perhaps, with due deference, suggest the chemical classification here shown (Table III.), which is derived directly from Table II. without recourse to transpositions other than the arrangement of the elements that fail between those of the inactive series in parallel columns. In order to bring those elements more or less chemically allied into horizontal alignment, the vertical columns are displaced downwards in sections, or the elements singly, as required. The arrows indicate displacements, and where a blank is shown without an arrow, it is suspected that an element will ultimately be found that will fit into it. Tellurium is out of place as usual, but the displacement of iodine to match bromine leaves a gap into which it would chemically fit. In this way a gap is provided for nitrogen.

There are some irregularities amongst the "rare earth" metals, particularly in the vertical series between cerium and lutecium. It is well known that great difficulty has arisen in the classification of these elements, and to get over this, "primary," "secondary," and "tertiary" tabular groupings have been proposed. I have in mind a table in Gooch and Walker's "Outlines of Inorganic Chemistry," which Browning gives (by permission) in his book, "Introduction to the Rarer Elements," 1908. Taking the group of rare earths in question that crystallise out in the order of their atomic weights (Urbain) Browning shows the following classifications:—

Lanthanum, primary series ..	Group III.
Cerium, primary series ..	" IV.
Praseodymium, tertiary series ..	" V.
Neodymium, tertiary series ..	" VI.
Samarium, tertiary series ..	" I.
Europium	(not shown)
Gadolinium, tertiary series ..	" III.
Terbium, tertiary series ..	" IV.
Dysprosium	(not shown)
Holmium	(not shown)
Erbium, tertiary series ..	" VI.
Thulium, tertiary series ..	" I.
Neoytterbium	(not shown)
Lutecium	(not shown)

The trivalent nature of these elements, &c., renders it difficult to assign all of them to a standard periodic table

without doing violence to it, although the atomic weights fit in exceedingly well. Some hold that a more intimate acquaintance with the properties of these elements will enable them to be placed in the standard table without much, if any, modification. At present, however, most of these elements require differentiating, and accordingly I have shown them in broken-face type in Table III.

It will be seen that the twin element, potassium, is in some respects out of place, and that oxygen, sulphur, fluorine, and chlorine would be more suitably situated alongside selenium and bromine. This optional or alternative position is shown. Similarly, it might be expedient to displace phosphorus and a few other elements to corresponding positions in the lower (repeating) part of the table, and so bring the arrangement more into agreement with existing sub-classifications. The table points to the advisability of assigning the elements to fixed places in space, strictly according to their properties, without necessarily attempting to closely assemble them.

If now the squares be coloured according as the elements are basic, acidic, or neutral in tendency in, say, blue, red, and purple (blue + red) non-homogeneous, whilst the inactive gases are coloured a homogeneous purple or violet, a very striking and instructive regularity is shown. The basic elements occupy a triangular area, and the acidic ones next to them occupy a similar area, the two together forming roughly a square. The elements of neutral tendency form a rectangle, neglecting potassium, which stands at one side; where the acidic elements repeat, an approximate square is formed, O, S, F, and Cl being retained in the upper position. Of course, the inactive gases would form a straight homogeneous coloured strip at the top. An even more beautiful effect is obtained by shading the above groups where they join along the borderland, to illustrate the gradual transition, or, as it were, overlapping of properties, just as colours blend in the spectrum. Indeed, the colour scheme may be so arranged as to suggest that all the elements are made from combinations of an acidic stuff (red) and alkaline stuff (blue) in varying proportions. (A third stuff functioning as a make-weight could be postulated if needs be, but the conception is only a fanciful one). When the two stuffs balance, no acidic or basic tendencies predominate, and the elements become neutral: such elements answering to the inactive or noble gases. The noble metals have very little red or blue stuff in excess, consequently they, or similarly constituted elements, function either as weak bases (lower oxides) or weak acids (higher oxides) according to circumstances. This is best illustrated by Table IV. (coloured supplement), but, of course, the application of colours is, after all, merely an obvious convention, since any periodic table can be coloured in some manner. The assignment of the "rare earths" (Ce to Lu) to Group IV. *en bloc* is, I believe, supported by Brauner (*Zeit. Anorg. Chem.*, 1902, xxxii., 18), Armstrong, and others.

This table brings out some of the properties and relations of the elements in a striking and comprehensive manner, and it is easy to trace resemblances by colour (diagonally) as well as by position (horizontally) or sequence (vertically), and some of the anomalies of the usual classifications disappear.

The terms "electro-positive" and "electro-negative" could be substituted for the purely chemical nomenclature, and it is on account of hydrogen being electro-positive that it is coloured pale blue, notwithstanding the arguments in favour of placing it in a line with fluorine. It may, in fact, be a sort of "transition" element between the alkaline metals and the inactive gases on one hand, and the acid-producing elements on the other, bearing in mind that the inactive elements, except argon, fall between those yielding acids and those yielding basic oxides. It is, perhaps, on this account that hydrogen assumes a double rôle in functioning in an alkaline capacity in ammonia, for example, and apparently in an acidic capacity in many other compounds, although the strong acid-giving property of oxygen, or of the body with which it (hydrogen) is

A PERIODIC ARRANGEMENT OF THE ELEMENTS—TABLE IV.

TYPE	ELEMENTS.										GROUP
Inactive (Neutral) Gases	St	He	Nt	Ne	Ar	Kr	Xe	RaEm	Z ¹	Z ²	O
	0·27	3·93	9·75	20·0	39·9	83·0	130·7	175·	216·	251·	
R ₂ O	H 1·0074	Li 7·00		Na 23·00		Rb 85·46	Cs 132·81			+	I
RO		Be 9·1		Mg 24·32	Ca 40·09	Sr 87·62	Ba 137·37		Ra 226·		II
RO ₂₋₃			B 11·0	Al 27·1	Sc 44·1	Yt 89·0	La 139·0				III
RO RH ₂₋₄			C 12·00	Si 28·3	Ti 48·1	Zr 90·5			Th 232·4		IV
RO ₂₋₆ RH ₃			* P 31·0	V 51·2	Nb 93·5			Ta 181·0			V
RO RH ₂₋₃			O 18·00	S 32·07	Cr 52·01	Mo 95·0		W 184·0	U 238·5		VI
RO RH ₂₋₇			F 19·0	Cl 35·46	Mn 54·93	Np 100·					VII
					Fe 55·85	Ru 101·7		Os 190·9			VIII
					Ni 58·68	Rh 102·9		Ir 193·1			VIII
					Co 58·97	Pd 106·7		Pt 195·0			VIII
R ₂ O				K 39·10	Cu 63·57	Ag 107·88		Au 197·2			I
RO					Zn 65·37	Cd 112·40		Hg 200·0			II
RO ₂₋₃					Ga 70·	In 114·8		Tl 204·0			III
RO ₂					Ge 72·5	Sn 119·0		Pb 207·1			IV
RO RH ₂₋₅					As 74·96	Sb 120·2		Bi 208·0			V
RO RH ₂₋₃					O 16·0	S 32·07	Se 79·2				VI
RO RH ₂₋₇					F 19·0	Cl 35·46	Br 79·92	I 126·92			VII
						Te 127·6	Ce 140·25				IV
							Pr 140·6				IV
							Nd 144·3				IV
* N=14·007 I.C.VALUE 1909.											
	1	2	4	8	16	17	Sa 150·4	?	?	?	IV
Totals not counting the inactive elements.							Eu 152·0				IV
" RO " - Groups = Higher saline oxides.							Gd 157·3				IV
" RH " - Groups = Higher gaseous hydrogen compounds.							Tb 159·2				IV
RARE ELEMENTS, which do not fit into the periodic table, are here shown displaced so as to fall into repeating groups.							Dy 162·5				IV
NEOYTTERBIUM, Urbain regards as a mixture, and the weight of Holmium lies between 162·5 and 167·							Ho				IV
BLUE = Basic or alkaline.							Er 157·				IV
RED = Acidic.							Tu 168·5				IV
BLUE + RED (non-homogeneous) = Tending towards neutrality							Ny 172·				IV
PURPLE (homogeneous) = Perfectly neutral							Lu 174·				IV

associated, throws much doubt on the rôle imputed to hydrogen.

It will, of course, be understood that the indication of types is, so far as given, according to Mendeleeff, and while some elements do not conform to the type indicated, others of the same group do, consequently the typical representations are justified.

It is difficult to obtain accurate colour values, and doubtless these could be improved.

This table in some respects is not unlike one suggested by Mendeleeff, which is shown on page 55 (1907 edition) of "Roscoe and Schorlemmer's Chemistry," vol. ii. Of course it is possible to trace back many resemblances. A few of these will be treated together under a separate head below.

Foreshadowings.—Odling (*Quarterly Journal of Science*, October, 1864) observed that in many cases the differences between the atomic weights of elements were 4 and multiples of 4, but that there were exceptions to this regularity, while Kremers, previously (1852), drew attention to similar differences between the equivalents of several elements, namely, that some were products of 4 with an odd integer, whilst others were products of 4 with an even integer. Wetherell (1904) published a Periodic Table in which 4 as a multiple functioned. Doubtless relationships of this kind have been noticed by others. In the present system, all the elements take up positions on the rungs of a ladder (series), 4 units apart, when it is projected on both sides of a zero. This evidently offers some explanation of the above-mentioned regularities. Likewise Rydberg's series is not unlike the present one, in that the odd and even numbers correspond with the projections above and below zero. Stoney's spiral, though it does not accurately co-ordinate the weights, involves elliptical functions, whilst in the present system the elliptical curves accurately co-ordinate the weights. No doubt many of the relations that I have pointed out are in a measure traceable in previously published methods, these involving some one feature in common. That geometrical relations have been previously found is apparent from a study of the subject, and it is not therefore surprising to find the geometric regularities I have given also, in a sense, foreshadowed.

A Summary.—The following is a brief statement of the principal features brought out by the enquiries so far made (see *CHEMICAL NEWS*, vol. xcix., pp. 148, 167, and 241; vol. c., pp. 37 and 120):—

1. The elements take up balanced positions in a simple series that passes through zero.
2. The "differences" assign the elements to places on elliptical curves (true ellipses).
3. The elliptical curves occur in uniform groups of nine, and take recurring numbers of elements.
4. The acidic elements are fairly uniformly distributed over the curves, as are likewise:
5. Those (non-acidic) giving peroxides, when this tendency is favoured.
6. The inactive elements are also symmetrically disposed on the curves, and
7. Two circles determine their position independently of the ellipses.
8. Nitrogen does not fit into the system, and
9. Beryllium (glucinum) falls away from any probable curve.
10. It is suggested that nitrogen, beryllium, iodine, and tellurium carry satellites, and
11. Perhaps some of the rare earth metals also carry satellites.
12. By the exclusion of nitrogen from the list of elements, on the assumption that it is built up from helium, the element Nt, and the satellite (these being of the inactive series), the active elements are marked off by the inactive ones into five groups, the number of elements comprising each increasing in geometrical progression. After 16 elements are passed, a tendency for this number (16) to repeat is noticed.

13. The hypothetical element Nt falls on a circle in the chart, and the value so obtained added to that of the satellite (deduced by trial methods), plus helium equals practically the latest atomic weight value assigned to nitrogen by the International Committee.
14. Plotting the inactive gases, including the element Nt on semi-logarithmic paper gives a curve that approximates to a straight line towards the finish, and
15. The possible values for two higher inactive elements than the Ra Em are found by extrapolation.
16. The theoretical positions of Ar, Fe, Br, and Ag on the chart, whereby these elements are on the curves in vertical alignment, calls for the same fraction for each, namely, 0.90 or 0.905. It has been observed that the second differences between these and other similarly situated elements are, in a few cases, in inverse geometric progression. The radio-active elements, in conjunction mainly with the inactive gases, have been arranged in these "quaternian" series.
17. The geometric grouping of the elements (*vide* 12) permits of a periodic arrangement by "displacements" that presents some practical features worth consideration.
18. There is a tendency for the more strongly magnetic elements to take up symmetrical or balanced positions in the table prepared from the curves. It should be noted that besides dysprosium, Tb and Gd give strongly magnetic oxides (B. Urban and G. Jantsch, *Comptes Rendus*, cxlvii., 1286).
19. There is also a "specific-heat sequence," indicating that when more is known of the specific heats under strictly comparable conditions, the values will bear a more exact relation to the positions of the elements on the curves.

In conclusion, it will be seen that the system affords a means of assigning the elements to the series according to their approximate weights, and the position of the "differences" determines the fractional part of the weight. By a study of certain regularities, it becomes possible not only to determine with some considerable degree of probability all the elements of the series, but also the fractions belonging to them. In this way, unknown elements should be fixed, and the weights of known ones corrected. It is perhaps premature to more than suggest this possible outcome until the refinements and methods of limitation are more fully developed. The "blank" extension of the list of the elements, far into the unknown, points to the possible existence of some that are too unstable to have more than a theoretical existence. Indeed, it is possible that the theoretical existence of the low weight element Nt, though from analogy stable, is merely an indication of a "tendency" which, owing to some abortive process of Nature, never, as it were, materialised. On the other hand, the extraordinary part nitrogen plays in colour phenomena (azo dyes) suggests that the satellite is in some way responsible for the brilliant colours produced, and beryllium, which I regard as carrying a satellite, should function in a somewhat similar capacity. Likewise certain rare earths may carry satellites—in particular ceria, which acts as an exciter and causes thoria to glow in the Bunsen flame with great brilliancy. This may be attributable to the vibrations of the satellite, or to the dynamic instability of the system due to its presence. The fact that radium gives off helium suggests that, if nitrogen has a satellite, it may also contain a helium atom, and this leaves a residue which answers to the element Nt. This reasoning is unsupported as yet by experimental facts, but nevertheless it may be of interest, especially since radio-active phenomena have widened our concept of the great possibilities in store in the field of physical chemistry. It is perhaps remarkable that the 1909 atomic weights should accord so well with mathematical theory. That there are many exceedingly exact determinations and coincidences which happen to be

nearer the truth than one might expect is very probable. It can almost be said, without drawing upon the imagination, that the atomic weights are exact mathematical functions.

7, Doughty Street, London, W.C.,
November, 1909.

A REVISION OF THE ATOMIC WEIGHTS OF IODINE AND SILVER.*

(PRELIMINARY PAPER).

By GREGORY PAUL BAXTER and GEO. STEPHEN TILLEY.

(Continued from p. 276).

The Specific Gravity of Iodine Pentoxide.—In order to find out exactly the buoyant effect of air upon the weight of the pentoxide an accurate knowledge of the specific gravity of the substance was necessary. The density was determined by displacement of kerosene of known specific gravity, by pentoxide which had been prepared as previously described by heating in a small platinum boat. The boat was weighed in a small weighing-bottle, and immediately after the weighing the boat was covered with kerosene in the bottle. The bottle was placed in a small vacuum desiccator, and the desiccator was kept exhausted with continual jarring until apparently every trace of air had been displaced from the powder. A special pycnometer stopper was next inserted in the bottle, and the pycnometer was set while immersed in a water-bath at 25° C. (For details of pycnometer and setting see Baxter and Hines, *Am. Chem. Journ.*, 1904, xxxi., 220).

The Specific Gravity of Iodine Pentoxide.

(Specific gravity of kerosene = 0.7655).

Weight of I ₂ O ₅ in vacuum.	Weight of displaced kerosene in vacuum.	Specific gravity of I ₂ O ₅ .
Grms.	Grm.	25°/4°.
5.5136	0.8811	4.790
5.2704	0.8393	4.807

Average 4.799 (a)

- (a) At 0° Ditte obtained the value 4.487. At 9° Kammerer obtained the value 4.799. Filhol found the density to be 4.250. Dammer, "Handb. der Anorg. Chem.," i., 560.

The vacuum correction for 1 apparent grm. of iodine pentoxide calculated from the above value for the density is +0.000106 grm., the weights being assumed to have the density 8.3 (Baxter, *Proc. Am. Acad.*, 1906, xlii., 209). Silver has been found to have the density 10.49 (Richards and Wells, *Pub. Carnegie Institution*, 1905, xxviii., 11), hence its vacuum correction is -0.000031.

A nearly new No. 10 Troemner balance was used in all the weighings. It was readily sensitive to one-fiftieth of a mgrm. The weights were carefully standardised to hundredths of a mgrm. by the method described by Richards (*Journ. Am. Chem. Soc.*, 1900, xxii., 144).

The Adsorption of Air by Iodine Pentoxide.—Since the pentoxide is formed by a process of double efflorescence, it must be extremely porous, with consequently an unusually large surface with relation to its weight. Hence it might be supposed that such a substance could adsorb appreciable amounts of gases, possibly even air. Stas, in the case of sublimed ammonium chloride, found that this substance does in fact adsorb air, and hence he weighed the chloride contained in an exhausted vessel ("Untersuchungen," Aronstein's translation, 1867, p. 56). This question was investigated with iodine pentoxide by determining the difference in weight of the substance in a vacuum and in air.

Two weighing-bottles were constructed with long very well ground stoppers, which terminated in stopcocks through which the tubes could be exhausted. These tubes were very closely of the same weight and of very nearly the same internal capacity. The tubes were first exhausted and compared in weight by substitution. Next, they were filled with dry air and again weighed, the weighings being carried out with the stopcocks open. Both steps were then repeated with essentially the same results.

Into one of the tubes was introduced about 25 grms. of carefully dried pentoxide, and both tubes were completely exhausted. When the tube containing the pentoxide was warmed to about 150° no perceptible quantity of gas was evolved. After the difference in weight of the exhausted tubes had been determined, they were again filled with dry air and weighed, and the process of exhausting the tubes and filling them with air was repeated. In all the weighings the tubes were treated as described in the case of the phosphorus pentoxide tubes.

	Grms.
I. Difference in weight of exhausted tubes ..	0.01405
I. Difference in weight of tubes filled with air ..	0.01395
I. Difference in air content of tubes	0.00010
II. Difference in weight of exhausted tubes ..	0.01415
II. Difference in weight of tubes filled with air ..	0.01397
II. Difference in air content of tubes	0.00018
Average difference in air content of tubes..	0.00014
Weight of tube with iodine pentoxide ..	58.6353
Weight of tube	32.7966
Weight of iodine pentoxide.. .. .	25.8387
I. Difference in weight of exhausted tubes, one containing iodine pentoxide	25.85120
I. Difference in weight of tubes filled with air at 19° C. and 758 mm.	25.84473
Difference	0.00647
Average difference in air content of empty tubes	0.00014
Air displaced by I ₂ O ₅ at 19° and 758 mm. .	0.00633
II. Difference in weight of exhausted tubes, one containing iodine pentoxide	25.85091
II. Difference in weight of tubes filled with air at 20° C. and 768 mm.	25.84430
Difference	0.00661
Average difference in weight of empty tubes	0.00014
Air displaced by I ₂ O ₅ at 20° and 768 mm...	0.00647
The same corrected to 19° and 758 mm. .	0.00641
Average weight of air displaced by I ₂ O ₅ at 19° and 758 mm.	0.00637
Weight of air displaced by I ₂ O ₅ at 19° and 758 mm. calculated from the density 4.799	0.00649

The agreement in the air displaced as determined experimentally, and as calculated from the observed density is as close as could be expected, showing that the vacuum correction determined above is correct. It is to be noted that if air is adsorbed by the powder the observed weight of air displaced would be less than that calculated from the density. This seems to be actually the case to a very slight degree.

(To be continued).

* Contribution from the Chemical Laboratory of Harvard College, From the *Journal of the American Chemical Society*, xxxi., No. 2.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 6th inst., Sir James Crichton-Browne, Treasurer and Vice-President in the Chair. Mr. J. H. Batty, Mr. T. Gibson Bowles, Mr. C. Broadbent, Captain F. S. Rose, Dr. H. Spitta, Mr. J. B. R. Swan, and Mr. J. S. Wilson were elected Members. Geh. Reg. Professor Dr. Otto N. Witt, President of the Chemical Society of Berlin, and Professor George E. Hale, Director of the Mount Wilson Solar Observatory of the Carnegie Institution, Washington, were elected Honorary Members.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, November 18th, 1909.

Prof. HAROLD B. DIXON, F.R.S., President, in the Chair.

(Concluded from p. 279).

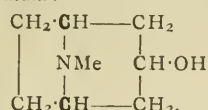
Of the following papers, those marked * were read :—

*258. "The Resolution of Asymmetrical Derivatives of Phosphoric Acid." By BERNARD DUNSTAN WILKINSON LUFF and FREDERIC STANLEY KIPPING.

A full account was given of the experiments which were briefly described in a preliminary note (vol. xxv., p. 203).

*259. "The Configuration of Tropine and ψ -Tropine, and the Resolution of Atropine." By MARMADUKE BARROW-CLIFF and FRANK TUTIN.

Tropine and ψ -tropine both possess a structure indicated by the following formula :—



It was considered by Willstätter (*Ber.*, 1900, xxxiii., 170) that the difference between these two bases is dependent on the relative positions in space of the hydroxyl and methyl groups.

In view of the fact that the tropine molecule contains two similar asymmetric carbon atoms (shown in heavy type), and could therefore exist in a racemic and an internally compensated form, it was thought that Willstätter's explanation should not be accepted unreservedly without further investigation. Experiments have therefore been conducted on the resolution of tropine and ψ -tropine by fractionally crystallising their salts with certain optically active acids, and it has been shown that both bases are internally compensated, thus confirming the view held by Willstätter regarding their relationship.

Atropine has been resolved by means of its d-camphorsulphonate, and salts of both the stereoisomeric hyoscyamines have been isolated in a state of purity. It has been shown that the latter bases, when in the form of their pure salts, have $[\alpha]_D^{20} \pm 32.1^\circ$, a value considerably higher than has previously been observed for hyoscyamine.

The following new salts were described :—Tropine d-camphorsulphonate (m. p. 236°), benzoyltropine d-camphorsulphonate (m. p. 240°), ψ -tropine d-camphorsulphonate (m. p. 224 – 226°), and d-bromocamphorsulphonate (m. p. 180°), benzoyl- ψ -tropine d-camphorsulphonate (m. p. 176 – 177°), and d-bromocamphorsulphonate (m. p. 190°), d- and l-hyoscyamine d-camphorsulphonates (m. p. 135° and 159° respectively), d-hyoscyamine auribromide (m. p. 160°), and picrate (m. p. 163°).

DISCUSSION.

Dr. LOWRY inquired whether, apart from the question of optical activity, the isomerism of tropine and ψ -tropine might not be compared with that of borneol and isoborneol, depending on the orientation of the CH·OH group relatively to the loops of the ring system.

Dr. W. H. MILLS pointed out that according to Willstätter's formula, although tropine contains two asymmetric carbon atoms, it is necessarily internally compensated and non-resolvable. For since three of the groups attached to the one asymmetric carbon atom are linked to the corresponding groups attached to the other, rearrangement of either of the asymmetric systems with respect to the other (so as to pass from, for example, a + + to a + – form) is impossible. The first asymmetric carbon atom is necessarily the mirror image of the second.

Since the planes of the piperidine and pyrrolidine rings are set at an angle, the relationship between tropine and ψ -tropine may be regarded as a case of *cis-trans*-isomerism,

the hydroxyl in the CH·OH group being in the one case on the same side of the plane of the piperidine ring as the pyrrolidine ring, and in the other case on the other side.

Further, as the nitrogen atom is common to two rings lying in two different planes, it, together with its three valencies, will presumably lie in a third plane roughly bisecting the angle between the other two. The nitrogen atom will thus lie out of the plane of the rest of the piperidine ring, and consequently the *cis*- or *trans*-relationship of the hydroxyl group can also be referred to it.

*260. "Adsorption in Relation to Gibbs's Theory. The Mercury Adsorbing Surface." By WILLIAM CUDMORE MCCULLAGH LEWIS.

The author has continued his experiments carried out with a view to verify experimentally Gibbs's expression for adsorption. Determinations were made with aniline, caffeine, mercuric sulphate, and sodium glycocholate. The presence of electrocapillary and electrostatic effects was discussed, and a general application was made to the case of the mercury drop-electrode.

DISCUSSION.

Mr. A. E. DUNSTAN asked the author whether the gelatinisation of the colloidal dyestuffs mentioned by him occurred during the process of dyeing; if so, what was the specific function of the mordant?

Mr. LEWIS, in reply to Dr. Cain as to the rôle of adsorption processes in dyeing, suggested dyeing of fibres as due to simultaneous solubility effects in the bulk of the fibre with adsorption on the surface. That the process of dyeing cannot be simply adsorption is evidenced by the fact that a simple adsorption process in the sense of Gibbs's theory is a reversible one; that is to say, if the fibre colour were simply due to adsorption, repeated washing should remove it. The fastness is probably due to gelatinisation (an irreversible process) on the surface of the fibre.

261. "The Electromotive Behaviour of Cuprous Oxide and Cupric Hydroxide in Alkaline Electrolytes." By ARTHUR JOHN ALLMAND.

Electrode systems containing copper, cupric hydroxide, and alkali are unstable, owing to the production of cuprous oxide. The following systems are stable :—

(a) Cu | Cu₂O alkali; (b) Pt | $\begin{array}{c} \text{Cu}(\text{HO})_2 \\ \text{Cu}_2\text{O} \end{array}$ alkali. The single potential differences involved in these systems were measured. Sodium and potassium hydroxide were used in both N- and N/10-concentration. The auxiliary electrodes used were calomel (N and N/10), as hydrogen electrodes are found to behave unsatisfactorily in alkaline electrolytes. From the results of the measurements, the solubility products of cupric hydroxide and cuprous oxide were calculated. Theoretical values for the hydrogen electrode in alkaline solution were assumed, and the E.M.F. of the cell Cu | Cu₂O alkali | $\begin{array}{c} \text{Pt} \\ \text{H}_2 \end{array}$ thus obtained.

From this was calculated the dissociation pressure of cuprous oxide at the ordinary temperature, and also the temperature at which cuprous oxide will dissociate when heated in air. The figures show satisfactory agreement with those calculated from thermal data by the use of Nernst's theorem. The influence of the size of grain of depolariser on potential measurements was recognised and emphasised.

262. "The Stereoisomeric Modifications of α B-Dibromobenzylacetophenone." By IDA SMEDLEY.

The action of bromine on benzylideneacetophenone was originally investigated by Claisen (*Ber.*, 1887, xx., 657), who added a molecular proportion of bromine to one of benzylideneacetophenone in chloroform solution; white needles melting at 157° separated, and were identified as the dibromo-additive product. Subsequently, the preparation of this substance was described by Wislicenus (*Annalen*, 1899, cccviii., 219), and later by Ruhemann (*Trans.*, 1904, lxxxv., 456). The latter observer points out that a better yield of the dibromo-compound is obtained if the bromination is carried out in carbon disulphide solution.

On mixing together molecular proportions of bromine and benzylideneacetophenone in chloroform solution, crystals separated, which melted at $157-158^{\circ}$ when re-crystallised from alcohol, and were identical with the dibromo-derivative previously described; the yield of this was from 70 to 80 per cent. On further concentrating the solution, white needles melting at 111° crystallised out; re-crystallisation from alcohol raised their melting-point to $112-113^{\circ}$.

0.1718 gave 0.3033 CO_2 and 0.0512 H_2O . $\text{C} = 48.15$; $\text{H} = 3.32$.

0.2115 gave 0.2158 AgBr . $\text{Br} = 43.37$.

0.2750 gave 0.2796 AgBr . $\text{Br} = 43.28$.

$\text{C}_{15}\text{H}_{12}\text{OBr}_2$ requires $\text{C} = 48.91$; $\text{H} = 3.26$; $\text{Br} = 43.47$ per cent.

This compound is therefore isomeric with the benzylideneacetophenone dibromide melting at 157° .

The more soluble isomeride (m. p. 113°) becomes discoloured if the temperature is raised above its melting-point, and shows signs of decomposition; after heating for some minutes at 180° , the dark coloured residue which solidified on cooling was pressed on a porous plate and crystallised from alcohol; white needles were obtained, which melted at $156-157^{\circ}$. The identity of this substance with the less soluble isomeride was confirmed by the mixed melting-point method.

263. "The Constituents of the Fruit of *Ecballium Elaterium*." By FREDERICK BELDING POWER and CHARLES WATSON MOORE.

The results obtained by an examination of elaterium and of the "elaterin" therein contained (*Pharm. Journ.*, 1909, [4], xxix., 501) have led the authors to undertake a complete investigation of the fruits of *Ecballium Elaterium*. One of the objects in view was to ascertain whether any evidence could be obtained in support of the statement by Berg (*Bull. Soc. Chim.*, 1897, [3], xvii., 85) that elaterin exists in these fruits in the form of a glucoside. The expressed juice of the fruit was found to contain, in accordance with a previous observation by Berg (*loc. cit.*), an enzyme which is capable of hydrolysing β -glucosides. For the purpose of a complete investigation, 27 kilograms of the fresh, nearly ripe fruit were employed. The alcoholic extract of this material yielded a quantity of resin, from which the following substances were isolated: a small amount of a hydrocarbon (m. p. 68°); a phytosterol, $\text{C}_{27}\text{H}_{46}\text{O}$ (m. p. 148° ; $[\alpha]_D + 3.2^{\circ}$); a substance (m. p. $258-260^{\circ}$) which appears to be related to ipuranol, $\text{C}_{23}\text{H}_{38}\text{O}_2(\text{OH})_2$; a mixture of fatty acids; and a product corresponding to the so-called "elaterin," the characters of which have previously been elucidated by the authors (*loc. cit.*). It is now proposed to designate the laevorotatory constituent of crude elaterin as α -elaterin, and the dextro-rotatory, physiologically active constituent as β -elaterin. The portion of the alcoholic extract which was soluble in water contained a quantity of inorganic salts and a sugar which yielded *d*-phenylglucosazone (m. p. 216°). It has been shown that the elaterin exists in *Ecballium* fruits in a free state, not in the form of a glucoside, and no evidence could be obtained of the presence of any glucosidic substance.

264. "3-Nitrodurene." By JOHN CANNELL CAIN.

As all endeavours to prepare mononitrodurene by the direct nitration of durene have hitherto proved unsuccessful—the dinitro-derivative always being obtained—Willstätter and Kubli have recently (*Ber.*, 1909, xlii., 4151) prepared aminodurene by first converting durene into the monobromo-derivative, then nitrating this to bromonitrodurene which is finally reduced with zinc dust and acetic and hydrochloric acids to aminodurene. These authors were able to prove that a small amount of nitrodurene is formed when iododurene is treated with silver nitrite, but as the nitrodurene is accompanied by much unchanged iodo-derivative, it could not be isolated in the pure state.

In continuation of his investigation of the derivatives of durene (*Ber.*, 1895, xxviii., 967), the present author, in the year 1895, prepared nitro- and amino-durene, but as the work was interrupted the results were not published.

3-Nitrodurene, $\text{C}_6\text{H}_4\text{Me}_2\cdot\text{NO}_2$, is readily obtained in good yield by diazotising 3-nitro-6-aminodurene (*loc. cit.*) in alcoholic solution and boiling until no more nitrogen is evolved. The solution is poured into water and distilled in a current of steam, when the pure nitro-hydrocarbon passes over as an oil which, on cooling, solidifies to colourless crystals melting at 70° . On boiling nitrodurene with tin and hydrochloric acid it is reduced to the amino-compound, which was, however, not further characterised.

265. "Chemical Affinity and Electrons." (Preliminary Note). By BERNHARD FLURSCHEIM.

In a recent paper it has been pointed out that the relations between molecular constitution and dissociation constants do not support the idea that atoms are linked by means of interposed electrons; since numerous organic reactions lead to the same conclusion, the author put forward the following alternative hypothesis:—

1. The atomic mass (or aggregate of positively and negatively charged particles) is surrounded by an ethereal layer or envelope, in which, by the action of free electrons within the atom, the form of energy called chemical affinity is induced similarly to the induction of molecular magnetism through Ampère currents.

2. The affinity thus induced varies, for different atoms, both in quantity and in quality. Its quantity depends on the capacity of the ethereal envelope, which is proportional to the surface of the uncombined and uncompressed atom. Its quality is a function of the electrical charges within the atom. If the latter contains equal amounts of positive and negative charges, no affinity is induced (inert gases; compare A. Michael, *Journ. Prakt. Chem.*, 1903, [2], lxxviii., 487). If positive or negative charges are in excess, the induced affinity assumes corresponding polarity. Its specific polarity, that is, the atom's polar affinity (A_p) per unit of its total affinity (A), corresponds with the proportion of the number (n) of excess of electrical charges (e) to the surface of the uncombined atom (s_u): $A_p/A = k \times ne/s_u$. The relative polarity of the atom is its specific polarity, expressed in fractions of maximal, that is electronic, polarity: $\Delta_p = A_p/A \times e$.

3. When two atoms are combined, their ethereal envelopes are contracted toward the point of linking, as a result of their mutual attraction. Thereby the atomic mass is compressed, until its resistance to compression produces an equilibrium (compare I. Traube, *Ber.*, 1907, xl., 729). This resistance is a function of the density of the uncombined atom, $F(d)$, and of its specific polarity, $F_1(A_p/A)$. Between the force of mutual attraction (Q) of two atoms, their uncombined volumes (v_u), and their volumes in combination (v), we accordingly have the relation—

$$v = \frac{k_1 \times v_u \times F(d) \times F_1(A_p/A)}{Q}$$

Q is the algebraic sum of the forces emanating from the polar (A_p) and non-polar (A_{np}) components of the affinities of the two atoms I. and II., and r being the distance of the atomic centres:—

$$Q = \frac{k_2 \times A_{npI} \times A_{npII} \pm k_3 \times A_{pI} \times A_{pII}}{r^2}$$

$\pm$ becomes $+$ for heteropolar and $-$ for isopolar atoms, in which latter case atomic combination may become labile (fluorine) or cease (many metals).

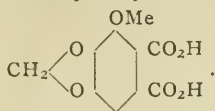
When one atom is linked to several others, Q and v for all are the results of an equilibrium (compare *Journ. Prakt. Chem.*, 1907, [2], lxxvi., 185).

4. Atoms transfer their own polarity to other atoms in proportion to the force with which they are linked to them.

5. These views are supported by ample evidence, especially by the changeable valency of strongly polar atoms, by substitution reactions, molecular volumes, and thermochemical constants. They are capable of throwing new light on various problems. Regarding migration velocity in electrolytes, for instance, it is seen that all existing calculations of ionic hydration based on conductivity measurements require modification; for they all assume that the electrodes attract the constant ionic charges, e , whereas only that part of e which is not bound by the atomic affinity of the solvent and solute can exert any attraction on the electrodes; and this free portion of the electronic charge varies from ion to ion, being the outcome of an equilibrium, as explained above.

266. "Synthesis of Cotarnic Acid." By WILLIAM HENRY PERKIN, jun., ROBERT ROBINSON, and FREDERICK THOMAS.

Starting with 5:6-methylenedioxy-1-hydrindone, the authors have succeeded in synthesising cotarnic acid in a way which clearly proves that its constitution is that represented by the usually accepted formula:—



267. "The Acyl-bornylamines. Part I. Fatty Bornylamides." By PERCY FARADAY FRANKLAND and FRED BARROW.

These compounds have been studied in connection with the relationship between chemical constitution and optical activity. The authors have prepared the formyl, acetyl, propionyl, and n-butyryl derivatives, and have determined their rotatory power in methyl and ethyl alcohol, in glacial acetic acid, and in pyridine solution respectively. The formyl and acetyl compounds have been previously prepared and optically examined in ethyl-alcoholic solution by Forster (*Trans.*, 1899, lxxv., 934, 1149).

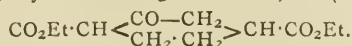
268. "The Acyl-bornylamines. Part II. Aromatic Bornylamides." By PERCY FARADAY FRANKLAND and FRED BARROW.

In continuation of the above work (preceding abstract), the authors have prepared the benzoyl, the o-, m-, and p-toluyll, and the o-, m-, and p-nitrobenzoyl derivatives. The optical activity was determined in methyl and ethyl alcohol, in glacial acetic acid, and in pyridine solution respectively. The benzoyl compound had been previously prepared by Forster (*Trans.*, 1898, lxxiii., 393), and its optical activity determined in ethyl-alcoholic solution.

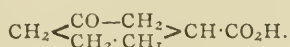
For purposes of comparison, some hitherto unpublished results obtained by one of the authors and Miss M. B. Thomas with the tartaronitroanilides (o-, m-, and p-) were described.

269. "Synthesis of cyclohexanone-3-carboxylic Acid." By MARY ELIZABETH DOBSON, JOHN FERNS, and WILLIAM HENRY PERKIN, jun.

The authors have prepared ethyl pentane- $\alpha,\alpha,\delta,\delta$ -tetracarboxylate, $\text{COEt}\cdot\text{CH}_2\cdot\text{C}(\text{CO}_2\text{Et})_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, and find that this ester reacts with sodium with the formation of ethyl cyclohexanone-3:6-dicarboxylate (I):—



I.



II.

On hydrolysis and elimination of carbon dioxide, this ester yields cyclohexanone-3-carboxylic acid (m. p. 73–75°) (II.), which had previously been prepared by Perkin and Tattersall (*Trans.*, 1907, xci., 480) from m-hydroxybenzoic acid by reduction and oxidation of the cyclohexanol-3-carboxylic acid so produced with chromic acid mixture.

PHYSICAL SOCIETY.

Ordinary Meeting, November 26th, 1909.

Dr. C. CHREE, F.R.S., President, in the Chair.

A PAPER ON "The Effective Resistance and Inductance of a Helical Coil" was read by Dr. J. W. NICHOLSON.

This paper deals with a determination of the effective resistance and inductance of a helical coil of great length, composed of thin wire, wound on a cylinder whose radius is large in comparison with that of the wire. The pitch of the winding is not small, so that the problem cannot be treated by the method of Cohen. The method employed depends upon the use of a type of "helical co-ordinates" defining the position of any point, and of the general theorem relating to orthogonal systems of co ordinates. A solution is obtained for the internal and external forces, corresponding to a given impressed electro-motive force, in the form of a Fourier series of which only the initial terms require calculation. The value of the effective current across any section is obtained, and thence the inductance and resistance. The results are of simple character, and are expressed in general in terms of the ber and bei functions of Lord Kelvin, whose results for a straight wire appear as a limiting case. Certain particular cases are worked out in detail and formulæ obtained in terms of elementary functions which are suitable for a very high or a low frequency. Their necessary limitations are also examined numerically. For a high frequency, it is found that the change of self-inductance due to twisting of the wire tends to vanish, and that the change of resistance tends towards a value independent of the frequency.

Dr. RUSSELL stated that the author's paper was most instructive and that he had done excellent pioneering mathematical work. This paper contained the first published attempt to get a solution of the very difficult problem of finding the effective resistance and inductance of a helical coil when traversed by high frequency currents. Previously, only cylindrical current sheets had been considered. He pointed out that, in the particular case when the wire was very thin, an approximate value of the inductance could be found by counting the linkages of the magnetic lines of force with the helical current. Even when the coil was of finite length this presented no great difficulty. In the author's problem, however, the wire was of finite thickness, and so the difficulties to be overcome were much greater. He considered that the author's solutions would prove very helpful to other workers in electro-magnetic theory.

Prof. C. H. LEES congratulated the author, and remarked that both the functions occurring in Equation 39 had been tabulated by Mr. Savidge. Prof. Lees indicated the form of the graphs of these functions.

The AUTHOR, in reply to Prof. Lees, said the tabulation of the functions referred to was most valuable.

A paper entitled "Ductile Materials under Combined Stress" was read by Mr. W. A. SCOBLE.

The author further considers the results from some earlier tests made on mild steel bars, $\frac{3}{8}$ inch diameter, and 30 inches effective length, under combined bending and torsion. It is pointed out that the yield-point is usually selected as the criterion of strength, because it is more easily determined than the elastic limit, it is less affected by special treatment of the material, and it is assumed that the failure of Hooke's Law between the elastic limit and the yield-point is due to local yielding. The elastic limit is the correct point, and is used throughout because the intermediate state mentioned above does not appear in bending. The results of tests on steel and copper tubes under combined bending and torsion are also given. All the results indicate that the maximum stress and maximum strain laws do not apply to ductile materials. The stress difference or shear stress law is approximately true, but there is, in each case, a deviation from the law which is

opposed to the other theories mentioned. The deviations from the shear stress law are considered. In an earlier paper the author suggested a formula for combined bending and torsion which allows for the fact that the bending moment is always greater than the torque. The internal friction hypothesis was also shown to be untenable. The three laws are now expressed in terms of the principal stresses, P_1 , P_2 , and P_3 , of which P_1 is the greatest and P_3 is the least. Guest's experiments proved that P_2 does not appreciably affect the failure of a material. The maximum stress law states that $P_1 = \text{constant}$; the maximum strain theory that $P_1 - \lambda P_3 = \text{constant}$, in which λ is Poisson's Ratio; and the stress difference or shear stress hypothesis is expressed in the form $P_1 - P_3 = \text{constant}$. In the general equation $P_1 - m P_3 = \text{constant}$, the value of " m " indicates which law is most nearly true for the material. The author's tests appear to be the only experiments in which bending was adopted, and for these the values of " m " are 1.57, 1.37, 1.26. The figures apply to different materials, but are all greater than unity.

The results obtained by other observers, who employed different methods and combinations of loading, are also examined. For Guest's steel tubes, " m " varies from 0.9 to 1.87; his copper tubes give 1.04 and 1.09. For brass tubes the values are 1.03 and 1.34. Smith's tests on steel, three series, show " m " to vary from 0.775 to 1.09.

The shear stress law appears to state the average behaviour of ductile materials, but there are considerable deviations from the law, which are usually opposed to the other theories. Other tests by the author indicate that brittle materials obey the maximum stress law, and it is therefore suggested that the value of " m " depends chiefly on the degree of ductility of the material considered, and to a lesser extent on the system of loading.

Prof. COKER congratulated the author on being able to present so many actual tests. Although many experiments had been carried out during the past ten years there was still difficulty in stating the law which was followed when a ductile material was subjected to stress. An initial difficulty was to determine whether the elastic limit or the yield-point should be selected as the criterion of strength. Guest had shown that for tension both points yielded similar results, but for combined stress the results were very different. He thought the elastic limit should be selected. With reference to the repeated loading of the tubes he thought more consistent results would have been obtained if a new tube had been used for each test. Although the results obtained threw light on the various theories they did not favour any one of them.

Mr. C. A. SMITH expressed his interest in the paper, and said he did not think much further progress would result from experiments on tubes. He enumerated the disadvantages connected with the use of tubes, and said he thought the case for the use of solid rods was proved. He did not think copper specimens were suitable for tests, as the same system of loading did not always give the same result. Mr. Smith pointed out that no reference had been made to non-axial loading. If the load was applied acentrically errors were introduced which should be allowed for. He thought it was advisable to work with as simple a formula as possible ($P_1 - P_3 = \text{const.}$), and to introduce a suitable constant for each different material.

Mr. SCOBLE, in reply to Prof. Coker, said that Guest used the yield-point as the criterion of strength. In his paper he (the author) had referred his stresses to the elastic limit; i.e., the point at which the strain ceased to be proportional to the stress. He had used solid bars of $\frac{3}{8}$ inch thickness because engineers required results on specimens as large as possible. He appreciated the advantage of using a simple law, but the results of his experiments did not follow any simple law.

A paper by Drs. W. MAKOWER and S. RUSS on "*The Recoil of Radium C from Radium B*" was read by Dr. Russ.

It has been shown in a previous paper, that during a radio-active transformation involving the expulsion of an

α -particle, the residue of the atom from which the α -particle has been expelled recoils in an opposite direction to that in which the α -particle is emitted, and can travel a considerable distance through a gas if the pressure is sufficiently low. A similar effect was also demonstrable in the case of the transformation of radium B into radium C, although this transformation is supposed to be accompanied by only β -rays. The phenomena associated with this recoil are studied in this paper.

In the first place it was found that it was only in certain circumstances that pure radium C free from radium B was projected from a plate coated with radium B and radium C. The reasons for this were twofold:—Firstly, only a very small fraction of the radium C produced from radium B escaped from the plate, so that even a small quantity of radium A on the plate was capable of emitting a comparatively large quantity of radium B. Secondly, the active deposit on a plate appears to be concentrated into heaps, so that radium C in breaking up mechanically carries with it some radium B. If, however, sufficient time is allowed after removing a plate from the emanation for radium A to completely decay, and if, further, sufficiently small quantities of deposit are used to avoid the formation of heaps, practically pure radium C is emitted.

The law according to which the radiation fell off with distance was also studied, and it was found that radium C is not emitted from an active plate equally in all directions, a greater quantity being emitted normally to the plate than in directions making an angle with the normal.

The absorption by air of radium C when it recoils from radium B was investigated. Although the experiments were difficult to perform owing to the ease with which the radium C is stopped by the air and owing to uncertain changes in the radiating power of the plate, it was possible to get some estimate of the penetration of radium C. It was found that about half the radium C projected from a plate was stopped by 2.5 cm. of air at a pressure of 0.04 mm. mercury. Since radium B emits only β -particles, the energy of recoil in this case should be less than one-millionth of the energy of recoil in a transformation in which an α particle is emitted. The fact that the penetration of radium C when it recoils is as much as one-fortieth of that previously found for radium A and radium B is therefore surprising.

All attempts to stop radium C by an electric field when it recoils have failed, indicating that radium C when formed from radium B either remains electrically neutral or, as is suggested by the absorption experiments described, the energy of a recoiling atom of radium C is for some unknown reason greater than has been supposed.

A paper on "*The Sun's Motion with respect to the Ether*" by Dr. C. V. BURTON was taken as read.

Notwithstanding the well-known "principle of relativity," it is theoretically possible to determine the motion of the solar system with respect to the ether from observations of the eclipses of Jupiter's satellites; and the possibility was indicated by Maxwell some thirty years ago. For convenience, the motion of the ether with respect to the sun may be called a wind, and the method proposed is based on the consideration that the tidings of an eclipse will travel towards us more rapidly when the Jovian system is to windward of us than when it is to leeward. The residual discrepancies between the observed and calculated times of eclipses have to be analysed for systematic differences depending on the direction in space of the straight line drawn from the earth to Jupiter, and formulæ are given for finding by the method of least squares the most probable values of a , b_1 , c_1 , the components of the sun's velocity with respect to the ether. The material available is to be found in Prof. R. A. Sampson's discussion of the Harvard photometric eclipse-observations; about 330 eclipses of Jupiter's satellite I being included.

In order to obtain a preliminary notion of the accuracy to be expected, a simplified system has been considered in which (for one thing) the eccentricity of the orbits was virtually neglected; and it appears that some advantage

is to be gained by taking the plane of Jupiter's orbit, rather than the ecliptic, as one of the coordinate planes. The axis of x is drawn from the sun's centre through the node of Jupiter's orbit, the axis of y lying also in that orbit, and the axis of z being perpendicular thereto. Taking 4.5 seconds as the "probable" discrepancy between theory and observation for a single eclipse, the following preliminary estimates are obtained:—

Probable error in a	$= 43.6$	km. per second.
" " b_1	$= 45.6$	"
" " c_1	$= 10,000$	"

The determination of the component perpendicular to Jupiter's orbit is perhaps too badly conditioned to be worth considering; the two components in the plane of Jupiter's orbit can be much better computed, and even if the velocities found do not exceed the probable limits of error, an upper limit to the numerical values of those components can be assigned.

ERRATUM.—P. 243, col. 1. The two opening sentences of Mr. Soddy's paper on "The Rays and Product of Uranium X" should be replaced by:—"Attempts have been made . . . to see whether there occurred the growth of a feeble α -radiation as the intense β -radiation decayed."

NOTICES OF BOOKS.

How to Study the Stars. By J. RUDAUX. Translated by A. H. KEANE, LL.D., F.R.G.S. London and Leipsic: T. Fisher Unwin. 1909.

ANY book which aims at rendering the study of the stars easier for the amateur would probably receive a cordial welcome, and there can be no doubt that many people with scientific tastes will greatly appreciate this work, the chief object of which is to show that there is no necessity for the purchase of expensive apparatus in order to get a great deal of pleasure from astronomical studies, and even to add to our knowledge of the universe. A general introduction gives a review in outline only of what the reader should know of the solar system, and in Part I. the various instruments for taking observations are described. The structure of telescopes, methods of mounting them, and different kinds of stands for visual observations are first described, and photographic appliances are also treated, various ingenious adaptations of apparatus for replacing the more complicated forms being suggested. The equipment of an observatory on a small scale is discussed, and though it seems a little ambitious for an amateur, still enthusiasm will often work wonders. Methods of taking observations are described in the second part of the book, and any difficulties likely to be encountered are fully explained, great care being taken to warn the beginner against discouragement because of apparent failure in his early attempts at observing and recording his observations. A short account is also given of the salient features of the major planets, which will greatly aid the student, and put him on the right track in his early work.

CORRESPONDENCE.

COMMERCIAL ANALYSES AND UNIVERSITIES.

To the Editor of the Chemical News.

SIR,—I should like to know if any of your readers can explain how it is that a Department of the Leeds University undertakes the analyses of samples of milk for a nominal fee, viz., determination of fat, 6d. per sample; determination of solids other than fat, 1s. per sample.

Does the undertaking of analytical work of any description for any section of the public, and receiving money in return, convert the University, which according to the Charter is a Teaching and Examining body, into a trading company? It is very doubtful if the people who contributed

so freely to the University ever contemplated such a proceeding as this.

It would be interesting to know the exact words of the Charter giving the University power to undertake analytical work for the public.

If a University Department can accept samples of milk for analysis, why cannot it undertake the analysis of water, beer, or anything else?—I am, &c.,

X.Y.Z.

Leeds, December 1st, 1909.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlix., No. 16, October 18, 1909.

Composition of Essence of Cloves.—H. Masson.—By the fractional distillation of essence of cloves and treatment of the fractions with phthalic anhydride in presence of pyridine the author has isolated methyl-*n*-amylcarbinol, methyl-*n*-heptylcarbinol, furfuralic alcohol, and benzyl alcohol. The presence of these alcohols confirms the observation that many natural essences contain among their constituents containing oxygen a higher oxidation product (ketone, aldehyde, or acid), and a neutral or reduced form (alcohol). The corresponding higher oxidation products have already been detected in essence of cloves.

MISCELLANEOUS.

Royal Institution.—The following are the lecture arrangements at the Royal Institution, before Easter:—Mr. W. Duddell, a Christmas course of six illustrated lectures on "Modern Electricity," adapted to a juvenile auditory—(1) First Principles, (2) Electrical Instruments, (3) Röntgen Rays, (4) The Generation of Electricity, (5) Electric Oscillations, (6) Electric Lighting; Prof. W. A. Herdman, three lectures on "The Cultivation of the Sea"; Rev. C. H. W. Johns, two lectures on "Assyriology"; Prof. F. W. Mott, Fullerian Professor of Physiology, R.I., six lectures on "The Emotions and their Expression"; Major Martin Hume, two lectures on "Europe's Debt to Mediæval Spain"; Prof. Silvanus P. Thompson, three lectures on "Illumination, Natural and Artificial"; Mr. A. J. Finberg, two lectures on "Turner"; Dr. H. Walford Davis, three lectures on "Music in Relation to other Arts"; Prof. Sir J. J. Thomson, Professor of Natural Philosophy, R.I., six lectures on "Electric Waves and the Electromagnetic Theory of Light." The Friday Evening Meetings will commence on January 21, when Prof. Sir James Dewar will deliver a Discourse on "Light Reactions at Low Temperatures." Succeeding Discourses will probably be given by the Rev. Canon Beeching, Prof. W. Bateson, Mr. C. E. S. Phillips, Prof. H. H. Turner, the Rt. Hon. Lord Rayleigh, Dr. Charles Chree, Dr. H. Brereton Baker, Prof. Sir J. J. Thomson, and other gentlemen.

The Andrew Carnegie Research Scholarship of the Iron and Steel Institute.—A Research Scholarship or Scholarships, of such value as may appear expedient to the Council of the Iron and Steel Institute from time to time, founded by Mr. Andrew Carnegie (Past-President), who has presented to the Iron and Steel Institute one hundred thousand dollars for the purpose, will be awarded annually, irrespective of sex or nationality, on the recommendation of the Council of the Institute. Candidates, who must be under thirty-five years of age, must apply on a special form before the end of February to the Secretary of the Institute. The object of this scheme of Scholarships is not to facilitate ordinary collegiate studies, but to enable students, who have passed through a college

curriculum or have been trained in industrial establishments, to conduct researches in the metallurgy of iron and steel and allied subjects, with the view of aiding its advance or its application to industry. There is no restriction as to the place of research which may be selected, whether university, technical school, or works, provided it be properly equipped for the prosecution of metallurgical investigations. The appointment to a Scholarship shall be for one year, but the Council may at their discretion renew the Scholarship for a further period instead of proceeding to a new election. The results of the research shall be communicated to the Iron and Steel Institute in the form of a Paper to be submitted to the Annual General Meeting of members, and if the Council consider the Paper to be of sufficient merit, the Andrew Carnegie Gold Medal shall be awarded to its author. Should the Paper in any year not be of sufficient merit, the Medal will not be awarded in that year.

Physical Society.—The Annual Exhibition of Physical Apparatus will be held on Tuesday, December 14, 1909, in the Afternoon from 3 to 6 p.m., and in the Evening from 7 to 10 p.m., at the Imperial College of Science, Imperial Institute Road, South Kensington. Tickets may be had on application to Mr. W. R. Cooper, 82, Victoria Street, London, S.W. Short discourses will be given as follows:—Prof. C. V. Boys, F.R.S., will show some Experiments on Soap Bubbles (at 4 and 8 p.m.). Prof. Silvanus P. Thompson, F.R.S., will show some Combinations of Mica and Selenite Crystals (at 9 p.m.). The following firms will be exhibiting:—Bausch and Lomb Optical Co.; British Radio-Telegraph and Telephone Co., Ltd.; Cambridge Scientific Instrument Co.; Casella and Co.; A. C. Cossor, Ltd.; H. W. Cox and Co.; G. Cussons, Ltd.; *The Daily Mirror*; J. H. Dallmeyer, Ltd.; Elliott Bros.; Everett, Edgcombe, and Co.; Gallenkamp and Co.; Gambrel Bros.; F. Harrison Glew; J. J. Griffin and Sons; Hicks and Co.; A. Hilger, Ltd.; Indiarubber, Gutta-percha, and Telegraph Works, Ltd.; Isenthal and Co.; Marconi's Wireless Telegraph Co.; Leslie Miller; Muirhead and Co.; Nalder Bros. and Co.; Nalder Bros. and Thompson; Negretti and Zambra; Newton and Co.; R. W. Paul; Pitkin and Co.; The Reason Manufacturing Co.; Ross, Ltd.; Siemens Bros. and Co., Ltd.; Snell and Tinsley; Strange and Graham; Synchronome Co.; Weston Electrical Instrument Co.; Carl Zeiss, Ltd. From the programme, of which we have received an advance proof, there appear to be many items of considerable interest to both Physicists and Electrical Engineers. We understand that invitations have been given to the Institution of Electrical Engineers, the Faraday Society, the Optical Society, and the Röntgen Society. Admission in all cases will be by ticket only, and therefore members of the Societies just mentioned desiring to attend the Exhibition should apply to the Secretary of the Society to which they belong.

MEETINGS FOR THE WEEK.

MONDAY, 13th.—Royal Society of Arts, 8. (Cantor Lectures). "Aeronautics," by C. C. Turner.

WEDNESDAY, 15th.—Royal Society of Arts, 8. "The Diamond Fields of Brazil," by H. Pearson.

— Microscopical, 8. "Measurement of Grayson's Ten-band Plate," by A. A. C. E. Merlin. "Convenient Form of Stand for Use as a Microcolorimeter and with Microspectroscope," by Dr. D. M. Ewell. "Life History of the Hessian Fly, with Notes on the Tenby Wheat Midge" by F. Enock.

THURSDAY, 16th.—Chemical, 8.30. "Production of Para-diazoimides from Alkyl- and Aryl-sulphonyl-para-diamines—A General Reaction," by G. T. Morgan and J. A. Pickard. "Organic Derivatives of Antimony—Part I., Tricamphorylantimonic Chloride and Triphenylantimonic Hydroxy-nitrate and -sulphate," by G. T. Morgan, Miss F. M. G. Micklethwait, and G. S. Whitby. "Constituents of *Rumex Eclouianus*," by F. Tutin and H. W. B. Clewer. "Influence of Non-electrolytes on the Solubility of Carbon Dioxide in Water," by F. L. Usher. "Ethyl Hydroxyisobutyrate," by W. Parry.

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THE CHEMICAL NEWS.

VOL C., No. 2612.

PHYSICAL AND CHEMICAL PROPERTIES OF ISOMERIC ORGANIC COMPOUNDS AS A FUNCTION OF THEIR CHEMICAL STRUCTURE.

By B. N. MENSCHUTKIN.

THE study of the relations existing between the properties of organic isomers and their structure was for more than twenty years the object of investigations of my father, the late Prof. N. Menschutkin; as these researches were published in many cases only in Russian (in the *Journal of the Russian Chemical Society*), and occasionally communicated solely to his hearers during the lectures on organic chemistry, they are but little known, and, as I had occasion to ascertain, almost totally so to English chemists. Being, however, of some importance and of interest to a considerable number of workers, I have taken it upon myself to communicate in this short paper the more important results of N. Menschutkin's work concerning the properties of aliphatic compounds; the physical and chemical properties of aromatic compounds I will leave for a future paper, whilst the influence of structure on the properties of polymethylenic compounds was fully discussed by my father some months before his death in a paper presented to the Chemical Society of London (N. Menschutkin, sen., "The Velocity of Chemical Change in the Polymethylene Series," *Journ. Chem. Soc.*, 1906, lxxix., 1532).

I. Physical Properties and Chemical Structure.

Of the physical properties, the temperatures of boiling-points formed the chief subject of N. Menschutkin's investigations, so that I will speak here more fully only about them. For these researches the isomeric organic substances were in many cases expressly prepared and purified with the utmost care; in some cases the data were taken from the papers of other chemists. (These data I have in some instances corrected when newer values were available; N. A. Menschutkin worked on this subject during the years 1890-1899). In the tables the isomeric organic substances are represented by structural formulæ showing the principal (normal) and side-chains of carbon atoms; as examples I have chosen mostly compounds containing five carbon atoms, as these are better known than those with a greater number of carbons, where many theoretically possible isomers are not yet prepared.

Beginning with the simplest compounds—saturated hydrocarbons—we have in Table I. the values for boiling-points of pentanes and hexanes (these last I also give here in order to better illustrate the generalities observed).

The analysis of these data shows that the hydrocarbons having the normal chain possess the highest boiling-point. The appearance of *one* side-chain lowers the temperature of the boiling-point; the greatest fall is observed in the case of the side-chain being nearest to the end carbon atom of the normal chain (as in the second and third hexanes). *Two* side-chains united with different carbon atoms produce a greater fall of the boiling-point, the lowest boiling-point belonging to the isomer where both side-chains are attached to the same penultimate carbon atom.

The boiling-points of other classes of aliphatic compounds, such as alcohols, iodides, amines, &c.—which, of course, can be all considered as substituted hydrocarbons—show similar regularities. Considering first compounds derived from the paraffins by substituting *one* hydrogen atom by the atom of another element (such as Cl, Br, I, &c.), or by a univalent group, such as OH, NH₂, COOH, &c., it is evident that the structure of such halides, alcohols, amines, acids, &c., as compared with the struc-

TABLE I.

Boiling-points of Pentanes.

CH ₃ .CH ₂ .CH ₂ .CH ₂ .CH ₃	36·3°
CH ₃ .CH ₂ .CH.CH ₃	30·4°
CH ₃	
CH ₃ .C.CH ₃	9°
CH ₃	

Boiling-points of Hexanes.

CH ₃ .CH ₂ .CH ₂ .CH ₂ .CH ₂ .CH ₃	69°
CH ₃ .CH ₂ .CH.CH ₂ .CH ₃	64°
CH ₃	
CH ₃ .CH ₂ .CH ₂ .CH.CH ₃	62°
CH ₃	
CH ₃ .CH.CH.CH ₃	58°
CH ₃ CH ₃	
CH ₃	
CH ₃ .C.CH.CH ₃	49·6°
CH ₃	

ture of hydrocarbons, presents a certain dissymmetry. In order to make evident at a glance this peculiarity and the structure of the different isomers, the substituting group is always placed at the end of the longest continuous chain (principal chain) of carbon atoms, whilst the order of carbon atoms is designated by Greek letters beginning with the end carbon of the principal chain (the C-atom united with the substituent); this arrangement is clearly seen in the following table containing the boiling-points of the eight isomeric amyl alcohols, whose side-chains are shown thus (CH₃):—

TABLE II.—Boiling-points of the Isomeric Amyl Alcohols.

Normal CH ₃ .CH ₂ .CH ₂ .CH ₂ .CH ₂ OH ..	138°
γ-CH ₃ .CH(CH ₃).CH ₂ .CH ₂ OH ..	130°
β-CH ₃ .CH ₂ .CH(CH ₃).CH ₂ OH ..	128°
α-CH ₃ .CH ₂ .CH ₂ .CH(CH ₃)OH ..	119°
α'-CH ₃ .CH ₂ .CH(C ₂ H ₅)OH ..	117°
α''-CH ₃ .CH(CH ₃).CH(CH ₃)OH ..	112·5°
ββ-CH ₃ .C(CH ₃) ₂ .CH ₂ OH ..	113°
αα-CH ₃ .CH ₂ .C(CH ₃) ₂ OH ..	102°

As in the hydrocarbons the highest boiling-point belongs to the alcohol possessing a normal chain; the boiling-points of other isomers are determined by the position of the side-chains with regard to the substituent (hydroxyl group). *One* side-chain produces the least effect if attached to the carbon atom most removed from the hydroxyl; the boiling-point of the γ-isomer is only 8° below that of the normal isomer. The nearer the single side-chain moves to the hydroxyl, the greater is the fall of temperature of boiling-point, the lowest boiling-point being observed where the side-chain is attached to the carbon atom united with the hydroxyl group (α- and α'-isomers). *Two* side-chains produce exactly the same effects, the maximal lowering of boiling-point being in this case noticed in the αα-isomer, where both side-chains are directly fastened to the last carbon atom. *Thus the position of the side-chains is the factor determining the temperature of boiling-point of alcohols, and not, as everywhere stated, the primary, secondary, or tertiary nature of the alcohol.* This rule—usually enunciated thus: primary alcohols boil higher than the secondary, and these higher than the tertiary (*vide*, for instance, "Modern Organic Chemistry," by Ch. A. Keane, 1909, p. 93)—must be abandoned, as it does not represent facts; a glance at the table of boiling-points of amyl alcohols shows that whereas the *primary* ββ alcohol boils at 113°, the *secondary* alcohols, α and α', boil considerably higher at 119° and 117°.

TABLE III.

	$x=I.$	$x=NH_2.$	$x=OOCCH_3.$	$x=COOH.$
Normal $CH_3.CH_2.CH_2.CH_2.CH_2x$	156°	104°	147·6°	205°
γ - $CH_3.CH(CH_3).CH_2.CH_2x$	148°	95°	139°	199·7°
β - $CH_3.CH_2.CH(CH_3).CH_2x$	145°	—	138°	196°
α - $CH_3.CH_2.CH_2.CH(CH_3)x$	144·5°	92°	134°	193°
α' - $CH_3.CH_2.CH(C_2H_5)x$	144·5°	90—91°	132°	190°
α (3- $CH_3.CH(CH_3).CH(CH_3)x$	138°	84°	125°	189—191°
$\beta\beta$ - $CH_3.C(CH_3)_2.CH_2x$	—	82°	126°	—
$\alpha\alpha$ - $CH_3.CH_2.C(CH_3)_2x$	127·5°	78·5°	124°	187°

The hexyl alcohols, of which at the present time 15 out of 17 possible isomers are known, also have the boiling-points completely determined by the position of the side-chains in respect to the hydroxyl group, in accordance with the regularities deduced for the isomeric amyl alcohols (N. Menshutkin, *Ber.*, 1897, xxx., 2784).

N. Menshutkin investigated also the boiling-points of many other isomeric organic compounds, and found everywhere the influence of the position of side-chains expressed in the same direction as we have seen for the alcohols—*i.e.*, the nearer the side chain (or side-chains) is to the substituent, the lower the boiling-point. For illustration, I give in Table III. the boiling-points of amyl iodides (the substituent x is equal to I), amyl amines ($x=NH_2$), acetic esters of amyl alcohols ($x=OOC.CH_3$), and capronic acids ($x=COOH$).

Other physical properties of the saturated aliphatic compounds, as far as known, are also dependent on the position of the side-chain (or side-chains) of the isomers with respect to the substituent; thus the melting-points are lowest in compounds with a normal chain and highest in the isomers having two side-chains in the position $\alpha\alpha$; the specific weights (whose values do not vary considerably from isomer to isomer) have apparently the greatest value in the case of absence of the side-chains (normal isomer), and lowest if two side-chains are present at the α -carbon ($\alpha\alpha$ -isomer).

The same relations of physical properties to the structure are observed in compounds formed by substitution of two hydrogen atoms of the hydrocarbons. Thus the isomeric butylene glycols and dibrombutylenes have the boiling-points given in Table IV.

TABLE IV.

	$x=OH.$	$x=Br.$
Normal $xCH_2.CH_2.CH_2.CH_2x$..	230°	196—197°
β - $xCH_2.CH(CH_3).CH_2x$..	—	—
α - $xCH(CH_3).CH_2.CH_2x$..	204°	174·5°
α - $xCH(C_2H_5).CH_2x$..	191—192°	165—166°
α' - $xCH(CH_3).CH(CH_3)x$..	184°	158°
$\alpha\alpha$ - $xC(CH_3)_2.CH_2x$..	177°	148—149°

Here, again, the highest boiling-point is characteristic for the compound with the normal chain, the appearance of one side-chain lowers the boiling-point; the lowest boiling-point is reached in the $\alpha\alpha$ -isomer, where two side-chains occupy the nearest possible position to the substituent x .

This work was carried out only with saturated aliphatic compounds; the unsaturated compounds containing five and more carbon atoms are known far too little to admit at present an exhaustive investigation of the influence of the different position of their side-chains on the physical properties.

II. Chemical Properties and the Structure.

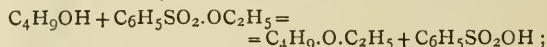
The relations between the chemical properties and the structure of isomeric organic compounds were studied by means of several reactions, which show a different velocity for different isomers. The earlier researches, namely, an investigation of the velocity of esterification of different alcohols by acetic acid ($ROH + CH_3.COOH = CH_3.COOR + H_2O$), are widely known; they enabled N. Menshutkin to draw the conclusion that the values of velocities of esterification

are greatest for primary alcohols, smaller for secondary, and smallest for tertiary ones. Afterwards, my father, for measuring the velocity of esterification, made use of the interaction between alcohols and acetic anhydride; the values obtained were more trustworthy, as the reaction takes place at a temperature not exceeding 100°, and an ester and acetic acid, but not water, are formed, $ROH + (CH_3.CO)_2O = CH_3.COOR + CH_3.COOH$. The results of these later investigations have shown that the velocity of this reaction depends not on the primary, secondary, and tertiary nature of the alcohol, but on the structure of its carbon chain; the alcohol with the normal chain has the greatest velocity; the appearance of one side-chain diminishes the velocity, and the value is smallest if this side-chain is attached to the same atom of carbon which is united to the group OH (α -isomer); two side-chains produce the same effect, the greatest fall of velocity being observed when both side-chains are attached to the α -carbon ($\alpha\alpha$ -isomer). As an illustration of these generalities, I give in Table V. the velocities of esterification of butyl alcohols by acetic anhydride (first column).

TABLE V.

	Velocity of esterification.	Velocity of etherification.
Normal $CH_3.CH_2.CH_2.CH_2OH$..	41·6	—
β - $CH_3.CH(CH_3).CH_2OH$..	35·9	21·4
α - $CH_3.CH_2.CH(CH_3)OH$..	13·2	16·1
$\alpha\alpha$ - $CH_3.(CH_3)_2COH$..	0·8	3·6

The second column of Table V. gives the velocities of etherification of the same butyl alcohols, measured by the action of the butyl alcohols on sulphobenzolic ether,—



the velocities of this reaction for the different isomers show the same relation to the position of the side-chains.

The same regularity holds good in the case of formation of amines, where the velocity of the action of allyl bromide (C_3H_5Br) on the eight isomeric amyl amines ($C_5H_{11}NH_2$) was determined; these velocities are given in Table VI.

TABLE VI.

Normal $CH_3.CH_2.CH_2.CH_2.CH_2NH_2$..	45·6
γ - $CH_3.CH(CH_3).CH_2.CH_2NH_2$..	35·9
β - $CH_3.CH_2.CH(CH_3).CH_2NH_2$..	33·2
α - $CH_3.CH_2.CH_2.CH(CH_3)NH_2$..	14·3
α' - $CH_3.CH_2.CH(C_2H_5)NH_2$..	8·1
α (3- $CH_3.CH(CH_3).CH(CH_3)NH_2$..	7·0
$\beta\beta$ - $CH_3.C(CH_3)_2.CH_2NH_2$..	9·5
$\alpha\alpha$ - $CH_3.CH_2.C(CH_3)_2NH_2$..	3·8

The influence of the position of side-chains was apparent in many other reactions; I will mention here only the action of ammonia or dimethylamine, $(CH_3)_2NH$, on the different isomeric valerianic acids (Table VII.).

TABLE VII.

Normal $CH_3.CH_2.CH_2.CH_2.COOH$..	—
β - $CH_3.CH(CH_3).CH_2.COOH$..	66·15
α - $CH_3.CH_2.CH(CH_3)COOH$..	29·8
$\alpha\alpha$ - $CH_3.(CH_3)_2CCOOH$..	Does not form an amide.

The smallest velocity in all such reactions is registered in the case of the isomer where the end carbon atom of the principal chain (having the substituent, α -atom) is attached to the side-chains; thus pinacene, $\text{HO.C(CH}_3)_2\text{—(CH}_3)_2\text{C.OH}$, and dimethylmalonic acid, $\text{HOOC.C(CH}_3)_2\text{.COOH}$, show the smallest velocities of formation of different derivatives.

In all the reactions mentioned above, the velocity of transformation has the greatest value for the normal isomer and the smallest for the $\alpha\alpha$ -isomer. Sometimes this order is reversed; the $\alpha\alpha$ -isomer (two side-chains at the α -carbon) shows the greatest velocity; this grows less as one side-chain disappears, and is smallest with the normal isomer. This is illustrated by the velocity of action of alcoholic potash on the different isomeric butyl iodides (Table VIII.).

TABLE VIII.

Normal $\text{CH}_3\text{.CH}_2\text{.CH}_2\text{.CH}_2\text{I}$	..	0.5
$\beta\text{-CH}_3\text{.CH(CH}_3\text{).CH}_2\text{I}$	..	1.42
$\alpha\text{-CH}_3\text{.CH}_2\text{.CH(CH}_3\text{)I}$	..	2.53
$\alpha\alpha\text{-CH}_3\text{.C(CH}_3)_2\text{I}$	..	4.0

Thus it will be seen that the physical and chemical properties of isomers are alike a function of their chemical structure, and depend on the position of the side-chains with regard to the carbon atoms of the principal chain. Several investigations which are at present conducted in our laboratory will, we expect, show further instances of the influence of structure on the properties of isomeric organic compounds.

Chemical Laboratory of the Polytechnical Institute,
St. Petersburg, Sosnowka,
October 18th, 1909

OPTICAL ACTIVITY OF THE ASYMMETRIC ATOM.

By A. E. EVEREST, B.Sc. (Priestley Research Scholar).

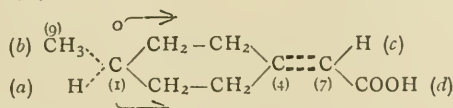
CONTRARY to the generally accepted theory that the optical activity of a substance is due to the presence in it of an asymmetric atom, Perkin, Pope, and Wallach, in a recent paper (*Chem. Soc. Trans.*, 1909, 1789) describe a substance—1-methylcyclohexylidene-4-acetic acid—as one containing no such asymmetric atom, yet capable of resolution into two optical enantiomorphs.

On the strength of this—in the author's words—"The first case of an optically active substance which possesses an enantiomorphous molecular configuration, although its constitutional formula contains no asymmetric atom," they decide that optical activity is due, not of necessity to the presence of such an atom, but to the asymmetry of the molecule.

It is unlikely that in such an interesting and important case their statements will be accepted without considerable criticism.

There appears to me to be at least one important point that yet remains to be cleared up before they can state that they have succeeded in obtaining an optically active substance containing no asymmetric atom.

They give the formula—



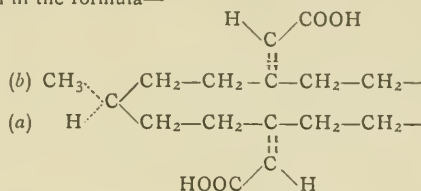
as representing the configuration of 1-methylcyclohexylidene-4-acetic acid, where, assuming the tetrahedron theory of distribution of the bonds of a carbon atom, continuous lines represent bonds in the plane of the paper; broken lines bonds in a plane perpendicular to the first, and passing through carbon atoms (1), (4), and (7).

Now, to me, it appears doubtful whether the carbon

atom (1) is not asymmetric, and thus the cause of the optical activity. For beyond the hydrogen atom (a) and the methyl group (b) the configuration of the remainder of the molecule must be considered in order to decide this question, and it is here that I think the authors assume too much when they take it that the configuration of the remainder of the molecule is the same when taken either way, relative to the carbon atom (1); for such is assumed if the carbon atom (1) is said to be not asymmetric.

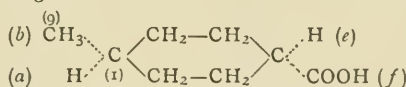
If we take the configuration of the molecule from the carbon atom (1) in the direction of the arrow ($\rightarrow$) we must come to the conclusion that it is not the same as when taken in the direction of the arrow ($\leftarrow$); for as we approach the carbon atom (4) following the arrow ($\rightarrow$) the hydrogen atom (c), in the same plane, comes in close proximity; whereas approaching from the direction of the arrow ($\leftarrow$), the carboxyl group, in the same plane, comes into close proximity. It is quite conceivable that this difference of configuration—already known to yield syn and anti isomers in many substances—may be sufficient to cause the carbon atom (1) to have asymmetric properties.

If instead of the ring formation we had two straight chain groups formed by swinging open the ring, to right and to left, the difference is perhaps more obvious. As shown in the formula—



It at least raises the point: Does the author's work prove that the differences in configuration pointed out above are sufficient to make the carbon atom (1) asymmetric? Or does it prove, as they claim, that the substance, though optically active, has no asymmetric atom?

An objection may be raised to these reasonings in that β -methylhexahydrobenzoic acid, which has not been found capable of resolution, at first sight appears according to them to contain the same asymmetric atom—also atom (4). But, taking the formula—



where the same representation of the bonds is taken, we see that now the hydrogen atom (e) and carboxyl group (f) are in the plane at right angles to the ring, hence approaching carbon atom (4) from either direction the positions of the groups are such that, at any point, the distance from either of them is the same, and thus the difference found in the former case is not observed. This also applies when testing the groups attached to carbon atom (1) to ascertain whether carbon atom (4) is asymmetric, and we conclude that neither atom (1) nor atom (4) is asymmetric.

Now, to clear up the matter, it at first sight appears only necessary to replace the hydrogen atom (c) of 1-methylcyclohexylidene-4-acetic acid by a carboxyl group, which would give the same configuration and spacial arrangement, whether considered in the direction of $\rightarrow$ or $\leftarrow$; but this at the same time destroys the asymmetry of the molecule, as it would then be asymmetrical about the plane through the hydrogen atom (a) and carbon atoms (1, 4, 7, and g).

Thus there remains some doubt whether this substance can truly be taken as an instance of an optically active compound having no asymmetric atom; until this point be settled, namely, whether such a difference in configuration as that pointed out above is sufficient to make such an atom as carbon atom (1) asymmetric.

NOTE ON THE INORGANIC CONSTITUENTS
OF TWO EGYPTIAN MUMMIES.

By PAUL HAAS, DSc., Ph.D.

THE following analyses of the inorganic constituents of two mummies were undertaken with the object of ascertaining, if possible, whether there was any difference in the method of embalming adopted in the two cases.

The two mummies, which date from the XII. Dynasty (about 2500 B.C.), were found in the same rock tomb* but in separate coffins; since the remains are those of two brothers the period which elapsed between the two burials cannot have been a very long one; the difference in the general appearance of the two mummies was, however, so marked as to suggest that the bodies had been embalmed in different ways.

The remains of mummy A which were analysed consisted of a very dry light brown powder, containing a quantity of well preserved pieces of muscle fibre and skin. The remains of mummy B, on the other hand, were dark brown and quite moist, and contained fragments of the scalp with the hair attached. Both the samples examined contained fragments of the material used as wrappings, but these were removed as completely as possible before analysis.

Examination of Mummy A.—A hot water extract of the powdered material had an acid reaction. On extracting the original substance with ether in a Soxhlet apparatus about 9 per cent of soluble material was removed; this substance had an acid reaction, and was soluble in caustic potash, but was not further identified.

After showing that the original substance was free from arsenic, antimony, or mercury by Reinsch's test, a quantity of the air-dried substance was incinerated on a platinum dish, and the constituents of the ash were then estimated; the amount of carbon dioxide, however, was estimated by weighing the gas evolved on treating the unaltered material with hydrochloric acid.

The results of the analysis are given below, together with the mean numbers obtained by Bunge (*Zeit. Phys. Chem.*, 1884, ix., 61) for the inorganic constituents of muscle.

Sample of mummy A.	Dried muscle (Bunge). ⁽¹⁾
Per cent.	Per cent.
CaO	4·83
K ₂ O	1·21
Na ₂ O	0·24
Fe ₂ O ₃	0·156
Al ₂ O ₃	0·134
CO ₂	2·64
SO ₃	1·91
P ₂ O ₅	1·57
Cl	0·22

- (a) The numbers quoted as Bunge's have been obtained by re-calculating the values actually given by him for undried muscle, on the assumption that the undried material contained 75 per cent of moisture, which is the amount usually accepted.
- (b) This number does not represent the amount of SO₃ actually present in muscle, but the amount which would be formed by the complete oxidation of all the sulphur in muscle.

The most striking discrepancy between the figures in the two columns is that in the case of the lime and of the carbon dioxide. The possibility of the high percentage of lime being due to the presence of bone is excluded by the fact that the ratio of CaO : P₂O₅ in bone is approximately 1·3 : 1, whereas it is in the present case 3 : 1. That the carbon dioxide was combined with the lime was shown by the fact that no soluble carbonate could be extracted by means of water, and, moreover, small fragments of calcium

carbonate were found in the material before it was powdered.

Since the addition of calcium carbonate, as such, could serve no useful purpose in the process of embalming, it is suggested that quicklime may have been originally placed in the coffin, and that in the course of time it became converted into calcium carbonate. Although it is, of course, difficult to make this assertion with confidence, it would appear to be at all events to some extent justified by the extraordinary dryness of the sample.

The presence of aluminium is noteworthy, since this metal is not a normal constituent of the body, but the fact that it was readily dissolved out of the ash of the incinerated material by dilute hydrochloric acid shows that it cannot have been present as a silicate.

Examination of Mummy B.—As already mentioned this sample was quite moist, and when dried in a steam oven lost 16 per cent of its weight; on exposure to the air, however, it rapidly gained in weight again.

An aqueous extract of the powdered material was also acid, but extraction with ether in this case only removed 3·5 per cent of soluble matter.

An analysis of the ash from this sample gave the following results:—

	Per cent.		Per cent.
CaO	0·90	CO ₂	traces
K ₂ O	0·77	SO ₃	2·99
Na ₂ O	9·03	P ₂ O ₅	0·42
Fe ₂ O ₃	0·27	Cl	1·89
Al ₂ O ₃	0·90	SiO ₂	5·80

From these numbers it appears that the inorganic acids are only sufficient to combine with about 4 per cent of soda, consequently the remaining 5 per cent must be combined with organic acids. This view was confirmed by titrating the amount of free alkali contained in an aqueous extract of the ash; it was found to be 4·5 per cent. Moreover, the residue remaining after extracting the original substance with ether gave on extraction with water a neutral solution, which contained the sodium salts of some organic acids which could be removed from the solution by acidifying with sulphuric acid and extracting with ether.

The aluminium, which was also found in this mummy, was present, to some extent, in a form soluble in water and was detected both in the bandages and in the rest of the substance analysed.

Conclusion.—While the use of sodium salts, either in the form of sodium chloride or in the form of "natron" or "nitrum" (said to be a mixture of carbonate, sulphate, and chloride of sodium), appears to have been a common practice in embalming, it seems clear that no sodium salts of any kind have been added to the material examined from mummy A. On the other hand, in the case of mummy B the use of some mixture such as "natron" would appear probable; it is true that there is only a trace of carbonate actually present now, and even that is not soluble in water, but the 4·5 per cent of soda shown to be combined with organic acids may have been originally added in the form of carbonate, which, in the course of time was decomposed by stronger organic acids produced by the decomposition of higher fatty acids. The presence of aluminium in mummy remains has not to the author's knowledge been previously recorded, but, in view of the astringent properties of aluminium salts, it is possible that they may have been employed during some part of the process of embalming.

Chemical Laboratory, St. Thomas's Hospital, S.E.

Presentation to Professor Koerner.—A Committee has been formed in Milan with the object of celebrating the seventieth birthday of Prof. Koerner. It is proposed to devote subscriptions to the following purposes:—(1) Foundation of a prize for work in pure and applied chemistry; (2) reprinting Prof. Koerner's works; (3) presentation of a gold medal to Prof. Koerner. The Treasurer of the Chemical Society will be glad to receive subscriptions, and will forward them to the Organising Committee.

* A detailed account of this tomb will be found in a monograph entitled "The Tomb of Two Brothers," published by the Manchester Museum.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, November 25th, 1909.

Sir ARCHIBALD GEIKIE, K.C.B., President in the Chair.

PAPERS were read as follows:—

"Change in Hue of Spectrum Colours by Dilution with White Light." By Sir W. DE W. ABNEY, K.C.B., F.R.S.

The author shows that by diluting the spectrum colours from the red to the green-blue, with moderate percentages of white light, their hue travels towards the yellow, the change being dependent on the amount of red and green existing in the white added. At a point near $\lambda 5780$ the hue remains unaltered by the addition of white, and it is towards this point in the spectrum that the colours on each side of it travel.

It is pointed out that this change in hue enables the relative amounts in green and red from $\lambda 5000$ to $\lambda 6000$ to be accurately determined.

"Nature of the Hydrogen Flocculi and their Structure at different Levels in the Solar Atmosphere." By Prof. G. E. HALE, For. Mem. R.S., and F. ELLERMAN.

"Boiling-point of Sulphur Corrected by Reference to New Observations on the Absolute Expansion of Mercury." By Prof. H. L. CALLENDAR, F.R.S., and H. MOSS.

"Refraction and Dispersion of Neon." By C. CUTHBERTSON, Fellow of University College, London, and MAUDE CUTHBERTSON.

The refractivities of neon (Ne_2) for different wave-lengths are found experimentally to be—

$\lambda \times 10^8$.	$\mu - 1 \times 10^6$.
6438	134.02
5461	134.30
4800	134.63

These can be expressed by the formula—

$$\mu - 1 = \frac{5.133 \times 10^{27}}{38517 \times 10^{27} - n^2};$$

where n is the frequency V/λ .

Owing to the feebleness of the dispersive power of neon, the accuracy of the value obtained for the dispersion is not to be relied on to less than 5 per cent.

Revised formulae for the refractive indices of helium, argon, krypton, and xenon are given, in the same form, which supersedes the use of Cauchy's formula.

"Refraction and Dispersion of Air, Oxygen, Nitrogen, and Hydrogen, and their Relations." By C. CUTHBERTSON and MAUDE CUTHBERTSON.

The refractivities of these gases for different wave-lengths are found experimentally to be:—

$\lambda \times 10^8$.	$(\mu - 1) \times 10^6$.			
	Air.	Oxygen.	Nitrogen.	Hydrogen.
6563	291.92	269.75	298.16	138.66
5790	292.98	270.99	—	139.33
5461	293.60	271.70	299.77	139.71
4861	295.11	273.45	301.21	140.64

Cauchy's formula of two terms is shown to be inadequate to express the dispersion of a gas, and a formula of Sellmeier's type is adopted—

$$\mu - 1 = \frac{C}{n_0^2 - n^2}.$$

In this form the refractivities of these gases are given by the constants shown in the table below.

Revised values of the indices of sulphur, phosphorus, and mercury, expressed in the same form, are also given, and it is shown that, on the electronic theory of dispersion, the relative numbers of "dispersion electrons" in hydrogen, oxygen, and nitrogen are as 1, 2, and 3 almost exactly;

in sulphur and phosphorus, to a less degree of accuracy, as 3 and 41. In mercury the number is in the neighbourhood of $4\frac{1}{2}$ to 5.

	$C \times 10^{-27}$.	$n_0^2 \times 10^{-27}$.	V.	C/V.
Air	4.6463	16125	—	—
Hydrogen ..	1.692	12409	1	1.692
Oxygen ..	3.397	12804	2	1.699
Nitrogen ..	5.0345	17095	3	1.678
Sulphur ..	4.808	4600	3	1.603
Phosphorus .	7.61	6534	$4\frac{1}{2}$	1.691
Mercury .. to	$\begin{Bmatrix} 7.82 \\ 18.371 \end{Bmatrix}$	$\begin{Bmatrix} 4360 \\ 4740 \end{Bmatrix}$	$\begin{Bmatrix} 4\frac{1}{2} \\ 5 \end{Bmatrix}$	$\begin{Bmatrix} 1.74 \\ 1.68 \end{Bmatrix}$

"Refraction and Dispersion of Sulphur Dioxide and Hydrogen Sulphide and their Relation to those of their Constituents." By C. CUTHBERTSON and MAUDE CUTHBERTSON.

The refractivities of sulphur dioxide for different wave-lengths are found experimentally to be:—

$\lambda \times 10^8$.	$(\mu - 1) \times 10^6$.
6700	656.40
6500	657.10
5800	661.26
5461	663.97
5000	668.63

These can be expressed in a formula of Sellmeier's type—

$$\mu - 1 = \frac{5.728 \times 10^{27}}{8929 \times 10^{27} - n^2}.$$

The refractivities of hydrogen sulphide for different wave-lengths are found experimentally to be:—

$\lambda \times 10^8$.	$(\mu - 1) \times 10^6$.
6563	636.22
5790	641.17
5461	644.03
4861	650.98

These can be expressed in the same form by—

$$\mu - 1 = \frac{4.834 \times 10^{27}}{7808 \times 10^{27} - n^2}.$$

The number of "dispersion electrons" in SO_2 is shown to be approximately equal to the sum of the numbers of "dispersion electrons" in S_2 and in O_2 .

The number of "dispersion electrons" in H_2S is, approximately, one more than the sum of the "dispersion electrons" in H_2 and in S_2 .

"Plapping Flight." By Prof. M. F. FITZGERALD.

"Crystalline Structure of Iron at High Temperatures." By WALTER ROSENHAIN, B.A., D.Sc., and J. C. W. HUMFREY, B.A., M.Sc.

The paper contains a preliminary account of observations on the effects of strain on iron at high temperatures.

Polished strips of nearly pure iron were heated *in vacuo*, and strained while hot, the central portions of the specimen attaining a temperature of about 1100°C . while the ends remained below visible redness.

Heating alone produced a surface pattern caused by a volume change in the metal when passing through the $\alpha = \beta$ transformation, and occasionally where the temperature was highest a slight tarnish which revealed the γ crystals.

Heating and straining *in vacuo* showed that at all temperatures attained deformation took place by means of slip on the gliding planes of the crystals; three distinct regions could, however, be distinguished, and temperature estimations by the method of Joly's melometer agreed with the identification of these regions with the α , β , and γ ranges of Roberts-Austen. This identification is supported by differential heating and cooling-curves given in the paper. In the α range the number and intensity of slip-bands increases rapidly with increasing temperature; at the transition-point—which is seen as a well-defined line across the specimen—the bands suddenly cease and remain minute during the β range; in the γ range the bands are

again numerous, but differ from those observed in the α range by their straightness and regularity and by the frequent occurrence of twin crystals. These observations are illustrated by three photo-micrographs.

The authors consider that their observations strongly support the allotropic theory of Roberts-Austen, particularly since they show that β iron, although at a higher temperature, is markedly harder and stronger than α iron. So much is this the case that when such a specimen was broken while hot, the fracture took place in the region of hottest α iron, just before the transition-point. The present observations also demonstrate the similarity of γ iron as found in nearly pure iron when heated, with the well known " γ " iron found in alloy steels.

"*Relation of Thallium to the Alkali Metals; a Study of Thallium-zinc Sulphate and Selenate.*" By A. E. H. TUTTON, M.A., D.Sc., F.R.S.

This communication contains the results of an investigation of the thallium salts of the zinc group of the monoclinic series $R_2M(S_{Se}O_4) \cdot 2.6H_2O$, analogous to the previous investigation of the simple rhombic salts of the series $R_2S_{Se}O_4$. The conclusions formed as the result of the latter research are fully confirmed and independently substantiated, as regards the relations of thallium to the alkali metals and ammonium, and the nature of the isomorphism existing between the salts of these various bases. A large number of crystal measurements and determinations of physical constants are recorded in the paper.

The main conclusion is that the morphological and physical properties of the crystals of these thallium double salts are such as quite entitle them to inclusion in the monoclinic isomorphous series of the general formula above given, but not to places in the more exclusive eutropic series within that isomorphous series. This eutropic inner series is confined to the salts whose interchangeable metals belong to the same family group of the periodic classification, namely, to those of potassium, rubidium, and cesium, the crystals of which exhibit the regular progression of angles and physical constants, according to the atomic weight of the metal, already pointed out by the author in previous communications. The crystals of the thallium salts resemble very closely those of the ammonium salts—which are also outside the eutropic series but are included in the isomorphous series—except as regards one outstanding specific property, that of refraction; for the crystals of the thallium double salts, like those of the simple sulphate and selenate of thallium, exhibit transcendent refractive power, which proves to be a characteristic property of the crystals of all the thallium salts yet studied by the author.

"*Nature of the Diffraction Figures due to the Helio-meter.*" By PHILIP FRANCIS EVERITT, University College, London.

This paper contains a discussion of the heliometer diffraction fringes. The matter is one of considerable importance, owing to its bearing on astronomical measurements taken with this instrument. A difficulty arose, owing to the appearance of these fringes in heliometer work on an artificial double star. It was then found that, although the subject had been discussed by Bessel, Hansen, and Gauss, a good photograph of the actual fringes obtained by Scheiner and Hirayama, and a series given for the calculation of the fringes by Bruns, all attempts at their actual numerical determination had failed, owing to the extremely slow convergence of the series adopted, at a small distance from the centre of the system. By the adoption of a semi-graphic method, and the use of mechanical integrators, it has been found possible to carry out the calculations needful, in order to obtain an accurate picture of the fringes. Photographs were taken of the fringes, and these, taken by the author, as well as the photograph taken by Scheiner and Hirayama, show a close

agreement with the calculated contours, and enable one to obtain the proportions of the central (non-elliptic) oval, with which observers are chiefly concerned. The close agreement between the calculated and theoretical values of the different parts of the system is a further proof that the old undulatory theory suffices to determine in practice the true dimensions of such diffraction figures.

"*Motional Effects of the Maxwell Ether-stress.*" By E. CUNNINGHAM, M.A.

There is an outstanding gap in electro-magnetic theory in respect to the attempt to reconcile the analysis of ethereal stress on the lines initiated by Maxwell with Newton's third law and with the law of the conservation of energy. In the present condition of theory there are assigned to the ether certain distributions of electro-magnetic energy and momentum. The hypothetical distribution of energy is necessarily associated with the Poynting vector which measures its rate of transference. The distribution of momentum is so defined that the rate of increase of the total amount within any given volume supposed at rest in the ether is equivalent to the resultant of the Maxwell stresses on the bounding surface. There is, however, no connection established between the transference of energy across an area and the stress across that area. Such a connection would require that it should be possible to assign to the medium in which stress and energy reside, a state of motion whereby the stresses might do the necessary amount of work; and this again would require the revision of the specification of stress, inasmuch as the ordinary expressions are computed for an element of surface which is at rest.

In the first section of the present paper it is shown that, if g is the intensity of electro-magnetic momentum ($[EH]/4\pi c$) and w the energy intensity ($[E^2 + H^2]/8\pi$), and the velocity v is taken in the direction of g of magnitude, such that $(c^2 + v^2)g = 2vW$, the same stress system which would account for the transfer of momentum will account for the transfer of energy, provided the ether is assumed to be moving with velocity v . The stress system is not the ordinary Maxwell one, but reduces to it in the electrostatic case. In this case it is known that the Maxwell stress may be analysed into a tension along the lines of force together with a uniform pressure at right angles to those lines. This property of the stress system, commonly given, is not true of the total stress (electric and magnetic) in the general field. It is shown, however, that the stress system obtained in the paper can always be reduced to this form. The direction of one of the principal stresses is always along the velocity v .

It is shown further that at the surface of a perfect reflector, stationary or moving, the velocity v is equal to that of the reflector combined with a velocity tangential to it; that is to say, a perfect reflector is analogous to an impenetrable boundary.

In the second part of the paper, a similar analysis is applied to radiation such as would exist in the interior of a cavity whose walls are moving, so that although the electric and magnetic forces vary extremely rapidly and in an irregular manner, there is necessarily a transfer of energy. Taking ϵ and γ as the mean values of the energy and momentum over intervals of time which are short as compared with those which are appreciable by mechanical means, but long as compared with the period of the irregular fluctuations which constitute natural radiation, it is found that the mechanical properties of the radiation may be represented as those of a continuous quasi-fluid, in which there is a definite pressure p at every point (the same in all directions) and a definite velocity v , the relations connecting the several quantities being:—

$$\begin{aligned} 3p &= \epsilon - v\gamma & \dots & \dots & \dots & 1. \\ c^2\gamma &= v(\epsilon + p) & \dots & \dots & \dots & 2. \end{aligned}$$

If a small volume V is followed in its motion with the quasi-fluid, it is found that the quantity—

$$p\sqrt{4/3}(c^2 - v^2) - 2/3 \dots \dots \dots$$

remains constant. If v^2 is neglected this becomes the known equation connecting the pressure and volume of steady radiation for adiabatic changes.

Finally, it is shown that if a state of the radiation differing slightly from the actual is conceived, and dQ is the difference in the energy of the small volume V , after allowing for the change due to mechanical causes, such as increase of momentum and volume, the condition that the expression dQ/T should be a perfect differential is that—

$$p(c^2 - v^2)^{-1/2} kT^{-1} \dots \dots \dots 4.$$

This with (3) involves the equation—

$$pV/T = \text{constant}.$$

"Aberrations of a Symmetrical Optical Instrument." By H. C. POCKLINGTON, M.A., D.Sc., F.R.S.

The doubly modified characteristic function is written down, and the singly modified function derived from it correct to terms of the fourth order of small quantities. This is transformed so as to take account of the existence of an exit pupil, and formulæ are found giving the aberrations for any position of the object and pupil in terms of the six coefficients of aberration of the system. Some relations are found between these aberrations, and connection is established with the methods of numerical calculation given in Whittaker's tract on "The Theory of Optical Instruments."

"Spectrum of Radium Emanation." By H. E. WATSON.

"Electric Conductivity and Density of Solutions of Hydrogen Fluoride." By Prof. E. G. HILL and Dr. A. P. SIKKAR.

"Sleeping Sickness in Uganda. Duration of the Infectivity of the Glossina palpalis after the removal of the Lakeshore Population." By Colonel Sir DAVID BRUCE, C.B., F.R.S., Captains A. E. HAMERTON and H. R. BATEMAN, R.A.M.C., and Captain F. P. MACKIE, I.M.S.

CHEMICAL SOCIETY.

Ordinary Meeting, December 2nd, 1909.

Prof. HAROLD B. DIXON, F.R.S., President, in the Chair.

MR. STANLEY OKELL was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. Gilbert Grahame Auchinleck, B.Sc., the Department of Agriculture, Grenada, W.I.; Fred Banister, B.Sc., the Grammar School, Doncaster; Howard Canton, 2, Gloucester Road, Regent's Park, N.W.; Herbert Hillier Hughes, B.Sc., 22, Ranelagh Road, Tottenham, N.; Douglas Wilshin Murch, Selby House, Victoria Road, Wednesbury; John James Beaumont Rees, B.Sc., Johannesburg College, S. Africa.

A ballot for the election of Fellows was held, and the following were declared duly elected:—A. K. Yegna Narayan Aiyer, M.A.; Jehangir Dhanjishaw Anklesaria; James Alexander Hadden Armstrong; Donald William Elsom Barker; Harold Baron, B.Sc.; Stanley Robert Best, M.Sc.; Hubert Frederick Bottomley; Henry Shaw Breakspear, B.A.; O. K. H. Burger, Ph.D.; Frank Ward Bury, B.Sc.; William Edward Callister, B.Sc.; William Gordon Carey; Hardee Chamblis, M.S., Ph.D.; Lakshami Chand, B.A., B.Sc.; James Ferguson Dawson, B.Sc.; Alfred Charles Dunningham, B.Sc.; Edward Charles Edgar, D.Sc.; Alfred Edge; Frederick Watson Edwards; Arthur James Ewins, B.Sc.; Edmund Victor Flack; George Peters Forester; Arthur Forshaw, M.Sc.; William Adolf Freymuth; Otto Fürstenhagen; George Pomeroy Furneaux, B.A.; Alexander David Gardiner; Henry Dent Gardner, jun., M.Sc.; Victor John Harding, M.Sc.; Arthur John Harvey; Robert Douglas Hendry; Eric John Holmyard; Benjamin Leech, M.A.; William Cudmore McCullagh Lewis, M.A.; Carl Olof Lundholm; John Muller, B.A.; Roland Victor Norris, M.Sc.; Joas

Cornelio Rodrigues Peixoto; Francis Hugh Ping; Charles Proud; Walter Ritchings, M.Sc.; Frederic William Robinson, B.Sc.; Pindi Das Sabherwal; Manindra Sinha; Spencer Boyd Oortis-Stanford; Guy Stephenson; George Bertram Stones, M.Sc.; James Thallon Strachan; Edward Walter Taplin; Charles Tapp; Hermann Thoms, Ph.D.; Joseph Grantley Tingle; Henry Thomas Tizard, B.A.; Herbert Turner, B.Sc.; Everard Cecil Van Essen; Nikolai Valiaschko; Charles Weizmann, D.Sc., Ph.D.; Richard Vernon Wheeler, D.Sc.; Herbert Ernest Williams; Joseph Pretty Wright; Roland Francis Young.

Of the following papers, those marked * were read:—

*270. *"A New Method for the Detection of Sodium, Cæsium, and Rubidium."* By WALTER CRAVEN BALL.

A solution of potassium bismuth nitrite, to which about 1 per cent of cæsium nitrate has been added, produces a yellow crystalline precipitate of—



with traces of a sodium salt. One part of sodium in presence of several thousands of potassium may thus be detected. Conversely, a solution of sodium bismuth nitrite is an excellent test for cæsium, and also for rubidium, if in not too great dilution.

DISCUSSION.

Mr. GRANT HOOPER said that the author referred to the precipitate which was thrown down when the reagent was exposed to oxidation by contact with the air, and in connection with the quantitative determination of sodium, he desired to ask how this precipitate from the reagent was affected by the 50 per cent acetone which was used to wash the sodium compound. It appeared as if there was some danger of the sodium, as determined under these conditions, coming out too high, and he observed that the last determination quoted by the author was, in fact, a trifle high.

*271. *"Note on Dr. Scott's Paper on the Molecular Weight of Tetraethylammonium Bromide and the Atomic Weight of Carbon."* By Sir EDWARD THORPE, C.B.

In determinations of atomic weight when the utmost attainable precision is aimed at, it is customary to reduce the weighings to what is styled a vacuum standard, and the reduction is almost invariably made by a calculation in which the relative densities of air, of the weights, and of the substance weighed are the data.

Marignac, as far back as 1843, pointed out that in certain cases, more particularly when the substance weighed was in a fine state of sub-division, this method might be attended with error, due to the tendency of finely-divided substances to occlude and condense air.

In a recent paper (*Comptes Rendus*, 1909, cxlix., 593), Guye and Zachariades have again drawn attention to this circumstance. They state that with certain substances the error may be so considerable as to affect materially the determination of the value of an atomic weight. By weighing successively in air and in a vacuum, the same mass of finely-divided material (from 20 to 50 grms. depending on its density), and comparing the weight so obtained with that deduced by the conventional method of calculation, they found that the method of calculation invariably over-corrects the weight, and that the difference between the weight actually observed and that obtained by calculation may amount to as much as, or even more than, 3/10,000.

The extent of the difference appears to depend on several factors. In the first place, it depends on the density of the salt, salts of low specific gravity always tending to show the greatest variation. But it also depends, and in a greater degree, on the physical state of the salt. Thus in the case of fused potassium chloride (sp. gr. 1.97) the difference shown by the salt in powder was 32 mgrms. per 100 grms.; in crystals it was 20 mgrms.; in large pieces it was only 5 mgrms. In the case of fused masses of salts of high density, and in that of fused metals, the

discrepancy, if observed, is extremely small, and in such cases is practically negligible.

In a recent communication to the Society (*Trans.*, 1909, xcv., 1200), Dr. Scott has given the results of a number of determinations of the molecular weight of tetraethylammonium bromide, from which he has deduced an atomic weight for carbon slightly in excess of that obtained by the combustion of carbon, of graphite, of pure charcoal, and that deduced by physico-chemical methods, all of which agree extremely well among themselves, and consistently point to the value $C = 12.00$.

The author believes the discrepancy observed by Dr. Scott may be largely, if not altogether, accounted for by the circumstance first pointed out by Marignac. Tetraethylammonium bromide is a salt of very low specific gravity (in a private communication Dr. Scott informed the author that he found it to be 1.35), and, as he mentions in his paper, it was employed by him in the state of a fine powder. Tetraethylammonium bromide is not included in the long list of substances experimented upon by Guye and Zachariades, and no direct data exist for determining the precise value of the correction to be applied to its so-called vacuum weight. There is, in fact, no substance in the list of so low a specific gravity as 1.35, but considering the nature of the salt it is reasonably certain that it must be as great as, and in all probability greater than, the maximum value hitherto found. The maximum value obtained by Guye and Zachariades was observed in the case of potassium nitrate (sp. gr. 2.09), namely, 33 mgrms. per 100 grms.

To ascertain what might be the influence of Marignac's correction in the case of Dr. Scott's observation, this value of 33 mgrms. may be applied. Dr. Scott found that, collectively, 44.17031 grms. of tetraethylammonium bromide were equivalent to 22.66675 grms. of silver. Applying Guye and Zachariades' number, the aggregate weight of the tetraethylammonium bromide would probably be at most 44.15573 grms., and on the assumption that the atomic weight of silver is 107.88, this would give the molecular weight of the salt as 210.154.

Taking the molecular weight of ammonium bromide as 97.962, on the basis of what is the accumulated testimony of the best determinations of the several atomic weights of its elements, we obtain 112.192 as the molecular weight of C_8H_{16} , whence we have $C = 12.008$.

It cannot therefore be regarded as established that the weight of the carbon atom in tetraethylammonium bromide, or in the group C_8H_{16} , is different from what it has been found to be in other carbon compounds.

The slight variation which Dr. Scott has observed will, in the author's opinion, be proved to be mainly, if not entirely, dependent upon the physical peculiarities of the salts he has employed.

*272. "The Correction of Weights of Substances Weighed in Air to Weights in a Vacuum." By ALEXANDER SCOTT.

Before passing to the consideration of the work of Marignac, and of Guye and Zachariades with reference to corrections to vacuum standards, whether by experiment or by calculation in the ordinary way, the author referred to the note on his determination of the atomic weight of carbon by Sir Edward Thorpe (see preceding paper). One point especially emphasised was that the value for C_8H_{16} is based on the difference between the molecular weights of tetraethylammonium bromide and ammonium bromide, both values being determined in the same way, with the same balance, pure silver, and the same set of carefully calibrated weights. It was thus hoped to eliminate any sources of error which might possibly be due either to the method or to personal equation. Therefore, if it is fair to deduct 33 mgrms. per 100 grms. of tetraethylammonium bromide, as Sir Edward has done, it would only be fair to take at least 22 mgrms. from 100 grms. of ammonium bromide, which would make for the 97.950 grms., which are equivalent to 107.88 of silver, 97.928 to be subtracted

from Sir Edward Thorpe's calculated value of 210.154, and this gives $C = 12.013$ (taking $H = 1.0075$). Furthermore, a similar correction ought to be applied to the combustion of carbon, for if any substance is capable of condensing air in its pores it is carbon. Applying the correction of 33 mgrms. per 100 grms. to the careful experiments of Van der Plaats, with sugar and paper charcoal, we get instead of $C = 12.004$, $C = 11.998$, so that the final effect of applying this correction all round is to increase rather than diminish the difference in the atomic weight of carbon as found by combustion methods and by the author's method.

As pointed out by Sir Edward Thorpe, Marignac (*Bibl. Univ.*, 1843, lxvi., 373) stated that there was a slight difference in the value of the correction to vacuum standards as found by the usual method of calculation from a knowledge of the densities of the substances involved and that found by direct weighing of these substances in a vacuum. This, however, is only very slight, as the following table shows. The author has added the last three columns to Marignac's table, taking the best values for the mean densities of the salts, and Marignac's value of 1.2 mgrms. for 1 cc. of air.

Salt.	Weight in air.	Weight in a vacuum.	Wt. of equal volume of air.	Density.	Error in mgrms.
$AgClO_3$	100	100.029	0.027	4.43	-2.0
$AgBrO_3$	100	100.021	0.023	5.21	+2.0
$KClO_3$	100	100.054	0.0515	2.33	-2.5
K_2CrO_3	100	100.044	0.0373	3.22	-6.7
KIO_3	100	100.030	0.308	3.89	+0.8
NH_4Cl	100	100.080	0.0792	1.515	-0.8

As Marignac's weighings are only given to mgrms., presumably his balance was only sensible to a mgrm., and an examination of the last columns shows, with the one exception of potassium bromate, that the evidence is quite as much against as in favour of his statement that any sensible error exists.

The recent paper of Guye and Zachariades (*Comptes Rendus*, 1909, cxlix., 593) gives a list of twenty-six substances, with their densities, and the errors stated to occur when 100 grms. of each are weighed in air in fine powder, and the correction for the displaced air applied in the usual way. This error they, like Marignac, ascribe to air condensed in the pores of the fine powders, although it is difficult to see why "hygroscopicité," as stated in their paper, should also enter into the question. These errors range from 33 mgrms. in the case of potassium nitrate to only 1 for copper oxide. For potassium chloride they give more data, stating that the errors are 5 mgrms. for fused lumps, 22 for crystals, and 32 mgrms. for fine powder. This last number means that 32 mgrms., or 27 cc. of air, are condensed in the pores of 100 grms. of finely-powdered potassium chloride, and therefore ought to be evolved with effervescence when the latter is dissolved in ordinary distilled water.

This statement seemed so extraordinary that the author weighed in a vacuum and in air potassium chloride in fused lumps, in crystals, and in fine powder, and observed practically no difference between the weights referred to a vacuum, whether found directly or by the ordinary method of calculation, with this precaution, however, that the calculation was made with the actual density of the air as determined at the time and not an average density as is too often done. The slight differences, which still seem to remain, would be in all probability completely removed had time permitted the preparation of an exact counterpoise to the vessel used to contain the salt. As, however, all this work has been carried out since Sir Edward Thorpe had most courteously sent the author a copy of the note communicated by him to the Society, it has not been possible to employ all the refinements which modern science suggests. The apparatus employed was a large test-tube, with cap carefully ground, and to which was sealed a good glass stopcock, both capable of keeping a vacuum for days, and a small flask similarly fitted. Their volumes were

respectively 186.5 and 82.16 cc. The large tube had to be weighed on a larger and less sensitive balance than the small flask. In addition to the three experiments of which the results are given in the table, two other experiments with crystals and fine powder were made with like results.

Weight of —	Fused salt.	Salt in crystals.	Salt in fine powder.
Tube, vacuum.	101.2616	101.2472	39.0418
Tube full of air	101.4876	101.4084	39.1424
Tube + KCl	215.5280	202.9178	106.8062
Tube + KCl + air. . . .	215.6840	203.0776	106.8648
KCl in a vacuum	114.2664	101.6706	67.7644
KCl in air.	114.1964	101.6092	67.7224
Air displaced	0.0700	0.0614	0.0420
Air along with KCl. . . .	0.1560	0.1598	0.0586
Total air	0.2260	0.2212	0.1006
1 cc. of air in mgrms. . .	1.212	1.186	1.23
Calculated correction for air	0.0703	0.0617	0.0423
Density of substance . .	1.9698	1.9527	1.9702
Error	0.0003	0.0003	0.0003

Mr. J. D. Kettle, chief assistant at the Davy-Faraday Laboratory, took finely powdered benzoic acid (a less dense substance than any of the substances mentioned above), and, on fusing 19.8 grms. of it in a vacuum and using a tube of approximately the same weight and volume as a counterpoise, was unable on a still more sensitive balance to detect the slightest change in weight, and no trace of gas was given off on fusion which could be detected by a mercury gauge any more than by the balance; as some of the salts in Guye and Zachariades' list were apparently hydrated, perhaps some of their results may have been due to loss of water, otherwise no explanation can be given of their most remarkable results. Until a detailed account of their work, giving the actual weighings, is available, further criticism is hardly called for.

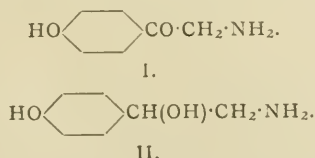
*273. "Synthesis of Hordenine, the Alkaloid from Barley." By GEORGE BARGER.

Hordenine, isolated by Léger (*Comptes Rendus*, 1906, cxlii., 108) from barley germs, and recognised by him as *p*-hydroxyphenylethyldimethylamine, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NMe}_2$, has now been synthesised from phenylethyl alcohol, which was successively converted into *β*-phenylethyl chloride and phenylethyldimethylamine: the phenolic hydroxyl was then introduced by successive nitration, reduction, and diazotisation.

The more obvious synthesis, by methylation of *p*-hydroxyphenylethylamine (Barger, *Trans.*, 1909, xcv., 1123), could not be carried out; by this means only hordenine methiodide was obtainable, but not hordenine itself.

*274. "Syntheses in the Epinephrine Series." By FRANK TUTIN, FREDERIC WILLIAM CATON, and ARCHIE CECIL OSBORN HANN.

The authors have prepared *ω*-amino-*p*-hydroxyacetophenone (I.) and *β*-*p*-dihydroxy-*β*-phenylethylamine (II).



Both of these compounds, when injected intravenously, considerably increase the blood pressure. The latter compound, however, is the more powerful, and, in its action, more closely resembles epinephrine.

The formation and properties of the above-mentioned bases (I. and II.) and of a number of new compounds were described.

(To be continued).

SOCIETY OF CHEMICAL INDUSTRY.
(LONDON SECTION).

Ordinary Meeting, December 9th, 1909.

Dr. J. LEWKOWITSCCH in the Chair.

"The Artificial Silk Industry." By W. P. DREAPER.

This industry has grown rapidly on the Continent since its inception in 1891. The present output is about 3,000,000 kilos. per annum, an increase of 500 per cent of that in 1896.

The nitro-cellulose product is still responsible for 50 per cent of the output, but the copper-ammonia, and viscose ones are making rapid progress. This product has not, up to the present time, come into competition with natural silk to any extent. Owing to the production of finer counts of superior strength and softness, it is likely to do so in the future.

The newer make is practically indistinguishable from natural silk in appearance. It is woven both warp and weft. The size of the individual filaments is even finer than that of natural silk. If it is a fact that the "true elasticity" of a cellulose filament is equal to that of real silk, there is no reason why a product may not be looked for in the future which will replace natural silk. The present strength of the yarns is improving rapidly, and is now from 50 to 70 per cent of that of real silk. Its "covering power" is also improving. It is made down to 40 deniers size, and will probably be made down to 25 deniers; a sample of the latter was shown for the first time, containing 60 filaments against 9 to 10 in the case of real silk.

FARADAY SOCIETY.

Annual General Meeting, November 30th, 1909.

THE following Officers and Council were elected to serve for the Session 1909-10:—

President—J. Swinburne, F.R.S., M.Inst.C.E.
Vice-Presidents—G. T. Beilby, F.R.S.; Sir R. A. Hadfield, F.R.S.; Prof. A. K. Huntington; Dr. Ludwig Mond, F.R.S.; Lord Rayleigh, O.M., F.R.S.; Prof. A. Schuster, F.R.S.; Ernest Solvay.
Treasurer—Dr. F. Mollwo Perkin.
Council E. J. Bevan, F.I.C.; Bertram Blount, F.I.C.; A. C. Claudet, M.I.M.M.; W. R. Cooper, M.A., B.Sc.; S. Z. de Ferranti, M.I.E.E.; F. W. Harbord, F.I.C.; W. Murray Morrison, M.I.C.E.; H. K. Picard, M.I.M.M.; J. L. F. Vogel, M.I.E.E.; N. T. M. Wilsmore, D.Sc.

Ordinary Meeting, November 30th, 1909.

Mr. JAMES SWINBURNE, F.R.S., President, in the Chair.

Dr. HENRY J. H. SAND read a paper "On the Electro-analytical Determination of Lead as Peroxide." (Already inserted).

Dr. N. T. M. Wilsmore read a paper by Mr. ARTHUR JAKUES, "On the Influence of Dissolved Gases on the Electrode Potential in the System of Silver—Silver Acetate, aq."

Variable values were found for the E.M.F. of the cell — $\text{Ag} | \text{Ag}_2\text{H}_3\text{O}_2, x\text{N} | \text{NH}_4\text{NO}_3, \text{sat.} | 0.1 \text{ N.E.}$, and the variations were traced to the presence of dissolved air in the silver acetate solution.

Measurements were made with saturated and 0.5 N silver acetate solutions saturated with hydrogen, oxygen, nitrogen, and carbon dioxide respectively, and reproducible values were obtained for the solution saturated with hydrogen which agreed with those calculated from the determinations of the E.P. of silver by G. N. Lewis and by Brislee. The values for solutions saturated with carbon dioxide also approximated to this.

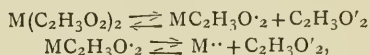
On blowing hydrogen into the solution saturated with

carbon dioxide the potential fell about 30 millivolts, then gradually rose to about the normal value. With oxygen and nitrogen equal values were obtained, about 20 millivolts below that found with hydrogen. In 0.01 N silver acetate saturated with hydrogen the values were not reproducible.

Similar measurements with 0.1 N silver nitrate and 0.5 mol. N lead acetate and lead nitrate showed that in these solutions the electrode potential is practically unaffected by the presence of dissolved gases.

MR. ARTHUR JAKES also contributed a paper entitled "*Contributions to the Study of Ionisation in Aqueous Solutions of Lead Acetate and Cadmium Acetate.*"

From measurements of electrode potentials in solutions of lead and cadmium acetates and their freezing-points, and the solubility of silver acetate in them, it appears that in dilute single solutions ionisation occurs chiefly, though not entirely, according to the scheme—



where M represents Pb or Cd.

Approximate values for the corresponding dissociation constants are calculated. In presence of excess of an alkali acetate a considerable amount of complex formation occurs, and on the assumption that the alkali metal does not take part in this, it appears that in not too concentrated solutions the complex-formation leads chiefly to the productions of the ions $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_3$ and $\text{Cd}(\text{C}_2\text{H}_3\text{O}_2)_3$ respectively. The dissociation constants of these complexes, namely—

$$K_3 = \frac{[\text{M}^{++}][\text{C}_2\text{H}_3\text{O}_2]_3}{[\text{M}(\text{C}_2\text{H}_3\text{O}_2)_3]},$$

cannot be greater than 10^{-5} and $5 \cdot 10^{-4}$ for lead and cadmium respectively. In strong alkali acetate solutions the values of $[\text{Pb}^{++}]$ and $[\text{Cd}^{++}]$ fall very fast with increasing alkali acetate concentration. This may be due to error in the values for the degree of dissociation.

The E.P. of cadmium is calculated to be -0.732 ± 0.006 volt against the 0.1 N.E. or -0.678 ± 0.006 volt against the 1.0 N.E. at 25°.

A paper entitled "*The Calorimetric Analysis of Hydrated Salts*" was communicated by Prof. F. G. DONNAN, Ph.D., and G. D. HOPE, Ph.D.

The authors point out that the interpretation of the heats of solution of hydrated and partially dehydrated salt given by Thomsen in his "*Thermochemische Untersuchungen*" is in various cases either erroneous or unsatisfactory.

It is shown that Thomsen's data for sodium carbonate indicate, when correctly interpreted, the existence of only the hydrates with 1, 7, and 10 mols. water per mol. anhydrous salt.

The author's experiments confirm this result.

In the case of copper sulphate, neither the experiments of Thomsen nor those of the authors indicate more than the existence of the hydrates $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot \text{H}_2\text{O}$, though the hydrate $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ is known to exist.

This calorimetric method may be employed as an aid in the discovery of the existence of salt hydrates, though it is probably neither so easy nor so reliable as other well-known methods.

RÖNTGEN SOCIETY.

At the December meeting of the Röntgen Society, Prof. A. W. PORTER, B.Sc., demonstrated some interesting new effects of electrical discharges on photographic plates which he has obtained during the last twelve months. He has allowed a discharge from an induction coil to spread itself out over the plates when a partial vacuum has been created around them, and he has found that at different stages of

pressure, from atmospheric to a state of complete vacuum, some new and remarkable appearances register themselves. The well-known fan-shaped figure obtained with a negative discharge at ordinary atmospheric pressure develops at first as the pressure is lowered, and afterwards disappears altogether. By changing the nature of the gas surrounding the plate new differences are noticed. Nitrogen, oxygen, carbon dioxide, and ammonia each give figures distinct from one another and from that of air. Prof. Porter explains the palm-leaf effect obtained in air at ordinary atmospheric pressure by suggesting that the same action takes place as in the burst of a firework ball. Each particle repels its neighbour, and the paths of the different particles are thus as widely divergent as possible. In the case of an electrical discharge over a plate the composite ion, he thinks, breaks up into smaller groups of ions, which have a mutually repellent action, and the palm-leaf figure is the result. He has obtained another type of effect by sending a blast of air across a plate, and by placing the plate between the poles of an electro-magnet. In such cases the main discharge which goes right across the plate is displaced. He believes that this part of the discharge consists of heated air which is made into a conductor, and this is blown aside by the blast of air or the magnetic field. Yet other remarkable figures were produced by making a triangle of copper or other metal form the electrode on the sensitive side of the plate. In the case of a positive discharge—i.e., one in which the triangle was made the positive terminal—there was a tendency for the streamers to come off from the corners of the plate, whereas in the case of a negative discharge they came from the sides of the plate, branching off almost at right angles. The fact that the negative discharge came off almost at right angles, said Prof. Porter, seemed to indicate that it was governed much more by the static conditions than the discharge of the positive.

In the course of the discussion, Mr. A. A. CAMPBELL SWINTON referred to the early experiments of Mr. John Brown, of Belfast, and the late Lord Armstrong along these lines, and expressed the opinion that the effect on the photographic plate was really due to the luminosity of the discharge acting photographically in the ordinary manner. This luminosity, though faint to the eye, was full of ultra violet rays, and was no doubt very actinic.

Prof. PORTER, in his reply after the discussion, said that he had been unable to trace any effect which depended upon the photographic plate. Whatever plate was used, from the slowest to the fastest, the results were the same, but immediately the air around the plate was varied a different effect was produced.

CORRESPONDENCE.

THE ATOMIC WEIGHTS AS MATHEMATICAL FUNCTIONS.

To the Editor of the Chemical News.

SIR,—I feel it my duty to point out that, while some of the coloured supplements are, in my opinion, very good, others undoubtedly have too much or too little red or blue in parts; particularly the proportions of red and blue, where superposed, are not as they should be. The blame rests with me in this matter.

I trust that those interested in the subject will correct the colour values with an ordinary red and blue pencil.

It has proved difficult to get uniform printings, but I hope that the attempt will be appreciated notwithstanding.—I am, &c.,

F. H. LORING.

7, Doughty Street, London, W.C.,
December 10th, 1909

OBITUARY.

DR. LUDWIG MOND.

WE regret to announce that Dr. Ludwig Mond, F.R.S., a founder of the great alkali firm of Brunner, Mond, and Co., an investigator whose researches have added materially to the progress of science, and one of the most distinguished industrial chemists of his generation, died early on Saturday morning at his house, "The Poplars," in Avenue Road, Regent's Park.

Scientific Discoveries.

Ludwig Mond was born on March 7, 1839, at Cassel, in Germany, where his father was a merchant. He attended the Polytechnic School of his native place, and thence went to study chemistry under Hermann Kolbe, at Marburg, and Robert Bunsen, at Heidelberg. His first contribution to industrial chemistry was a method, which was used among other places at works at Newcastle and by the Fennants at Glasgow, for recovering the sulphur which was lost as calcium sulphide in the black-ash waste of the Leblanc soda process. Coming to England in 1862, he obtained a post at the chemical works of Messrs. Hutchinson and Earle, of Widnes, and there he worked out the practical application of his patent. Two years later he returned to the Continent and erected an alkali manufactory on the Leblanc system at Utrecht; but in 1867 he came back to England, which thenceforth became his permanent home. Up to about this time the world's demand for alkali had been satisfied by means of the Leblanc process, according to which salt is first treated with sulphuric acid, and then the resulting sodium sulphate is converted by roasting with coal and limestone to a product known as black-ash, from which carbonate of soda is removed by lixiviation, calcium sulphide remaining as a waste product. But for many years chemists had been trying to devise a commercially satisfactory method of utilising a reaction whereby, without the intervention of sulphur in any form, carbonate of soda is produced by the action of carbonic acid on brine saturated with gaseous ammonia; but little except failure had to be recorded until the Belgian chemist Ernest Solvay turned his attention to the matter, and, after meeting many difficulties, succeeded in constructing apparatus for working this ammonia soda process on a commercial scale at Couillet. In 1872 Mond inspected his works, and as a result of what he saw determined to introduce the process into England.

Nearly ten years before, when he was at Widnes, he had formed a friendship with Mr. J. T. (now Sir John) Brunner, and the two had agreed that, if opportunity offered, they would enter into partnership as chemical manufacturers. Solvay's achievement seemed to provide the opportunity. The partnership was constituted in 1873, sufficient capital was raised, in small amounts, to purchase the Winnington Hall estate on the Weaver, near Northwich, over the Cheshire salt deposits, and towards the end of the year the manufacture of alkali was begun under licenses from Solvay. For a time technical difficulties threatened to overwhelm the enterprise, but these were ultimately overcome by Mond's skill and knowledge, and from the beginning of 1875 development was rapid. In particular he devoted his attention to the removal of one great obstacle that stood in the way of the commercial success of the ammonia soda process—the recovery of the ammonia used as a reagent. Later also he attacked the problem of recovering the chlorine lost in the form of chloride of calcium, a waste material which, however, is now finding some application as a dressing to prevent dust on roads; and in 1896 he was able to claim that by his improvements he had attained his object of rendering the ammonia process an effective competitor with the Leblanc process in the production of bleaching-powder.

Another question to which Dr. Mond applied himself was that of the economical utilisation of fuel; and the outcome of his work on this subject, which began about

1879, was the invention of the system of producing power-gas known by his name. Cheap bituminous slack is treated in a gas-producer, where it is acted upon by an air blast charged with superheated steam. The fuel gases produced are then brought in contact with dilute sulphuric acid, when the ammonia present in them combines with the acid to produce sulphate of ammonia, which is continuously withdrawn from the circulating gases, the residuum then being used for purposes of lighting and heating or for internal combustion engines. At every stage of the process the most ingenious arrangements are introduced to utilise the thermal energy and prevent waste, and the volume of power-gas produced from each ton of fuel is stated to be about 150,000 cubic feet, sufficient to develop about 2000 indicated horse-power hours when consumed in gas engines. The sulphate of ammonia is of course a valuable substance for manurial purposes, and the economic advantages of the process partly depend on the amounts realised by its sale. It follows that the price obtained for it is an important factor, and one obstacle to a widely extended use of Mond gas therefore appears to be the danger that owing to increased production the price obtained for the sulphate might fall to an unremunerative level. In South Staffordshire the gas is laid on to factories from mains like ordinary illuminating gas.

Many experiments were also made by Dr. Mond in the hope of utilising Grove's gas battery for the production of electricity on an industrial scale; and though they did not enable him to achieve success in this particular object, they incidentally led him to the discovery of a valuable process for the extraction of nickel from its ores. Being anxious to use the hydrogen contained in producer-gas for the purposes of the battery, he sought for some means of removing the accompanying carbon monoxide; and in the course of the work, in which Carl Langer and Friedriche Quincke acted as his collaborators, it was noticed that the latter gas combines with nickel to form a substance now known as nickel carbonyl, which is remarkable as being a gaseous compound formed at a temperature below a red heat, and which affords a means by which nickel can be, as it were, volatilised and separated from other metals. This compound, which was brought to the notice of the Chemical Society in 1890, was the first representative of an entirely new group of chemical compounds, other members of which Mond subsequently discovered in the shape of iron, cobalt, and other carbonyls. It is readily formed, it was found, when the gas and the nickel are brought into contact at about 250° C., and is decomposed, with production of metallic nickel, at 200° C., both these reactions thus being accomplished at very moderate temperatures—a point of enormous importance in relation to their commercial application. On the basis of these observations a large experimental plant for the reduction of nickel from its ores was erected at Smethwick in 1892, and in time the process was developed into the successful form in which it is now worked by the Mond Nickel Company at Swansea.

Recognition of Dr. Mond's attainments was not lacking. He was Grand Cordon of the Crown of Italy, and a member of the Accademia dei Lincei; and he received honorary degrees from Padua, Heidelberg, Victoria, and Oxford Universities. He was President of the Society of Chemical Industry in 1889, and of the Chemical Section of the British Association at its Liverpool meeting in 1896; and he was chosen President of the Chemical Society this year, though for reasons of health he was unable to serve. Another distinction which he enjoyed was election to the Athenæum Club under Rule II. in 1898.

Benefactions to Science.

Dr. Mond was a munificent benefactor of scientific research. It was through him that the Royal Society, of which he became a Fellow in 1891, was enabled to bring out its international catalogue of scientific papers, and he made generous contributions in aid of the investigations carried out at the Royal Institution. Further, he trans-

ferred to the managers of the latter body, under a trust endowment, the freehold of the house adjoining its premises in Albermarle Street, for the purposes of a laboratory for research in pure and applied science, to be known as the Davy-Faraday Laboratory of the Royal Institution. This laboratory, which was formally opened by King Edward (then Prince of Wales) in 1896, he not only furnished with the most modern apparatus, but he also placed in the hands of the managers of the Royal Institution an ample annual endowment sufficient to maintain it in a state of thorough efficiency.

Dr. Mond's Pictures.

Not only was Dr. Mond an eminent man of science and a leader in chemical industry, the extent of whose achievements may be gauged from the fact that the companies associated with his patents in England have a capital exceeding £5,000,000, but he was also devoted to certain branches of art, and especially to early Italian painting. Some twenty-five years ago he began to form a collection, his own taste being helped by excellent advice from leading authorities here and on the Continent, especially Dr. J. P. Richter. In due time his gallery of old Italian masters came to be one of the most important of the newer collections in England, and for many years he freely lent his treasures to the winter exhibitions of the Royal Academy. The pictures which he valued most highly were the early "Crucifixion," by Raphael, and the "Mother and Child," a late work of Titian, both of which he acquired at the Dudley sale in 1892. For the Raphael he paid what was then thought the very high price of 10,000 guineas, and for the Titian, a very masterly but slight performance, about a quarter of that sum. Other pictures of importance possessed by him were a "Holy Family," by Mantegna, a "Flora," by Palma Vecchio, and two panels with scenes from the life of San Zenobio, by Botticelli: while masters such as Fra Bartolommeo, Garofalo, Bazzi, and Bissolo were also well represented in his gallery.

Dr. Mond married in 1866 Frida Loewenthal, his cousin. Of his two sons the elder, Robert, of Combe Bank, Sevenoaks, who inherits his father's scientific and artistic tastes, graduated with honours in the Natural Sciences Tripos from Peterhouse, Cambridge, in 1888, and is honorary secretary of the Davy-Faraday Research Laboratory; while the younger, Alfred, was elected M.P. in the Radical interest for the city of Chester at the general election of 1906.

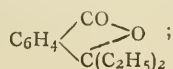
The funeral took place at the St. Pancras Cemetery, East Finchley, on Tuesday.—*The Times*, December 13, 1909.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

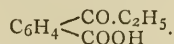
NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Berichte der Deutschen Chemischen Gesellschaft. Vol. xlii., No. 14, 1909.

Action of Organic Magnesium Compounds on Dicarboxylic Acids and a Method of Converting a —COOH Group into —CO.R.—H. Simonis and K. Arand.—When alkyl magnesium bromide even in large excess acts on phthalic acid only one carboxyl group is attacked, yielding a CO.R group, and this reaction provides a new method of synthesising ketone acids from dicarboxylic acids. From *o*-phthalic acid and ethyl magnesium bromide two compounds are obtained: diethylphthalide,—



and propiophenone orthocarboxylic acid,—



Propyl magnesium bromide with phthalic acid yields the homologues 3,3-dipropyl phthalide and butyrophenone ortho-carboxylic acid.

Reaction between Sulphuryl Chloride and Ammonia.—Fritz Ephraim and Franz Michel.—When sulphuryl chloride acts on ammonia, the latter being present in excess, the products are quite different from those obtained when excess of sulphuryl chloride is used. Neither sulphamide nor sulphimide is formed in any quantity, but the only products are those obtained secondarily by the decomposition of sulphamide. Substances containing long chains are chiefly formed, such as $\text{NH}_2\cdot\text{SO}_2\cdot\text{NH}\cdot\text{SO}_2\cdot\text{NH}\cdot\text{SO}_2\cdot\text{NH}\cdot\text{SO}_2\cdot\text{NH}_2$. It has been proved that this substance, for instance, is not a mixture of one molecule of sulphamide $\text{SO}_2(\text{NH}_2)_2$ with one molecule of trisulphimide.

Iridium.—A. Gutbier and M. Riess.—Concentrated hydrobromic acid when added to a solution of iridium chloride gives a dark blue solution on warming. If bromine vapour is allowed to act on the liquid the compound H_2IrBr_6 is obtained in the form of a bright blue solution. The same result can be obtained by mixing concentrated alkali bromide solution with iridium chloride solution at the temperature of the water-bath. Hexachloroiridates are formed when alkali bromide solutions act on excess of iridium chloride. These crystalline chlorosalts are converted into hexabromoiridates by dissolving them in hot dilute hydrobromic acid and allowing bromine vapour to act on the filtrate while it cools. The hexabromoiridates are anhydrous and stable in air, but are decomposed when gently heated, giving off bromine vapour.

Action of Ozone on Metals and the Cause of Passivity.—W. Manchot.—Ozone can be used to detect very small traces of oxide on the surface of a metal. If silver is heated to about 200° in air it reacts with ozone, and therefore must be covered with a very fine layer of oxide. The passivity of a metal is due to the formation on its surface of a layer of oxide which may be so thin that it cannot be detected by any known means, except by ozone. If a certain time has elapsed since the formation of the layer of oxide the metal behaves towards ozone as if it were not covered with oxide. The passivity of a metal also gradually disappears, and apparently the contact between the oxide and the metal is loosened by degrees.

Oxidation of Trivalent Platinum.—Lothar Wöhler and F. Martin.—When finely powdered platinum tetrachloride is heated to 390° in pure chlorine a residue of PtCl_3 is left; a more convenient method of preparing it is to heat the lower chloride PtCl_2 to 390–400° in chlorine for about five hours. The sesquichloride is a black or greenish powder which is intermediate between the higher and lower chlorides as regards solubility in water. With boiling water it gives an acid solution, in which the presence of $\text{H}_2\text{PtCl}_3\text{O}$ may be assumed. The sesquichloride is almost insoluble in concentrated hydrochloric acid at the temperature of the room, but dissolves on warming, and cannot be obtained again on evaporating off the hydrochloric acid. Pt_2O_3 is obtained when platinum sesquichloride is treated with boiling soda solution or with strong caustic potash. It is a brown substance which is stable towards oxygen. It appears to be capable of existence only in the form of a solid solution in excess of PtO . In the hydrated state it occupies a middle position as regards properties between the dioxide and the lower oxide.

MEETINGS FOR THE WEEK.

MONDAY, 20th.—Royal Society of Arts, 8. (Cantor Lectures). "Aeronautics," by C. C. Turner.

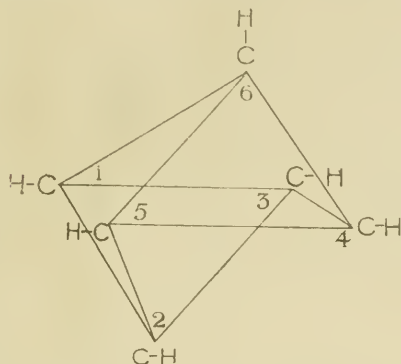
THE CHEMICAL NEWS

VOL. C., No. 2613.

A NEW SPACE REPRESENTATION OF THE BENZENE MOLECULE.

By J. C. EARL.

THE following representation of the benzene nucleus is, I believe, entirely new. It consists of an octahedron with three sides removed, the remaining sides representing bonds linking the carbon atoms.

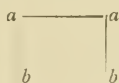


All the carbon atoms are equivalent, each being linked to three other carbon atoms and one hydrogen atom.

The nucleus may be numbered as shown, when it will be seen to consist of three incomplete squares in three planes, viz. :—

- The incomplete square 2, 1, 6, 4 in the plane of the paper.
- The incomplete square 6, 5, 2, 3 in a vertical plane at right angles to the paper.
- The incomplete square 1, 3, 4, 5 in a horizontal plane at right angles to the paper.

If we examine one of these incomplete squares separately, we find that the two positions *a, a*, are equal, and also that the two positions *b, b*, are equal.



Considering the whole figure again, we find that each carbon atom is at an *a* position of one incomplete square, and at a *b* position of another.

Only one mono-substitution product can be obtained as all the hydrogen atoms are equivalent.

In regard to di-substitution products we need only work out possible isomers with regard to one plane, as what applies to one will apply to others.

Ortho-substitution in the plane 2, 1, 6, 4 can take place in the positions 1, 2; 1, 6; 6, 4. The positions 1 and 2 and 6 and 4 are similarly related, so according to theory two ortho-disubstitution products can be formed.

Only one meta-disubstitution product can be formed, e.g., 1, 4 or 6, 2. Only one para-disubstitution product can be formed, e.g., 1, 5. Of additive hydro-derivatives, di-, tetra-, and hexa-hydro-derivatives can exist without rupturing the ring.

By drawing 1 and 5 farther away from one another, so that 1, 5, 6 and 2 come all into the same plane and the plane figure 1, 5, 6, 2 becomes a square, the prism representation of Ladenburg is obtained.

This octahedral formula differs from others in that the diagonals do not come into the question.

23, Lorne Road, Stroud Green.

THE NITROGEN COMPOUNDS IN RAIN AND SNOW.

By FRANK T. SHUTT, M.A., F.I.C.

AT the meeting of the Royal Society of Canada in 1907 the writer presented a short paper entitled "The Fertilising Value of Snow," in which were given the amounts of the various nitrogen compounds found to be contained in the snow as it fell near Ottawa during the latter half of the winter 1906-7. Nitrogen present as free ammonia, albumenoid ammonia, and as nitrates and nitrites had been determined, and the average total nitrogen content of the snow found to be 0.471 part per million, of which the largest part was in the form of free ammonia. With the average snowfall at Ottawa, 90 inches, our results showed that the winter's snow furnished, approximately, per acre, 1 lb. of nitrogen valuable as a fertiliser.

This investigation has been uninterruptedly continued, samples representative of each fall of rain and snow that furnished a sufficient quantity for examination, being collected and analysed, so that now we can place on record the data for the year ending February 29th, 1908. In all, 78 samples were analysed, 46 of rain and 32 of snow. The results obtained for each month have been averaged, and from these averages the total monthly amounts of nitrogen in the various compounds, per acre, calculated, using therefore the precipitation data recorded on the Experimental Farm. This has furnished approximately the amount of nitrogen in the snow and rain during the twelve months.

The monthly totals for the precipitation, the average amounts of nitrogen present in the three forms, and the pounds of nitrogen per acre so supplied, are given in Table I.

One or two of the more important facts brought out by the foregoing data may be briefly considered.

1. The amount of nitrogen in the rain and snow at Ottawa during the year was 4.323 lbs. per acre. Of this, 74 per cent, or 3.199 lbs., was present as ammonia and ammonium salts, and 26 per cent, or 1.124 lbs., as nitrates and nitrites.

In this connection it is of particular interest to note that in a paper entitled "Composition of Rain-water at Rothamsted" (*Journal of Agricultural Science*, Vol. I., Part 3, October, 1905), Dr. N. H. J. Miller reports that the average amount of nitrogen in the forms of ammonia and nitric (and nitrous) acid in the Rothamsted (Herts, England) rainfall during thirteen years ending 1900-1, is 3.84 lbs. per acre per annum, and the relative amounts of ammoniacal and nitric nitrogen were 70 and 30 per cent, respectively, of the total.

During the year ending February 29th, 1908, practically twice as much water fell as rain as in the form of snow—24.05 inches of rain and 13.3 (equivalent to 133 inches of snow) as snow, and we estimate that of the total nitrogen furnished per acre during this period (4.323 lbs.), approximately 75 per cent, or 3.243 lbs., was present in the rain, and 25 per cent, or 1.080 lbs., in the snow.

Finally, it will be of interest to compare rain and snow from the point of view of their nitrogen content (Table II.).

In free and albumenoid ammonia the rain, it will be seen, is much richer than the snow, but as regards nitric nitrogen there is not much difference. The total nitrogen content of the rain is almost twice that of the snow, which, if the atmosphere is fairly constant in respect to nitrogen compounds throughout the year, would go to show that rain possesses a greater solvent power, is a more thorough cleansing agent, than snow.

Considering the proportion or distribution of the nitrogen

TABLE I.—Rain and Snow at Ottawa for Year ending February 29th, 1908.

Month and year.	Precipitation in inches.			Nitrogen, parts per million.				Pounds of nitrogen per acre.
	Rain.	Snow.	Total as inches of rain.	In free ammonia.	In albumenoid ammonia.	In nitrates and nitrites.	Total.	
1907—March	1'55	11'50	2'70	2'25	0'049	0'193	0'467	0'286
April	2'59	7'25	3'32	0'320	0'056	0'120	0'496	0'372
(a) May	1'56	7'50	2'31	0'082	0'033	0'065	0'180	0'094
June	2'20	—	2'20	0'490	0'156	0'147	0'793	0'395
July	3'73	—	3'73	0'275	0'117	0'145	0'537	0'454
August	1'13	—	1'13	0'369	0'102	0'114	0'585	0'150
September ..	3'32	—	3'32	0'503	0'129	0'137	0'769	0'579
October	2'70	1'00	2'80	0'434	0'085	0'193	0'712	0'452
November ..	3'37	5'50	3'92	0'349	0'063	0'064	0'476	0'423
December ..	0'81	34'75	4'28	0'349	0'096	0'171	0'616	0'597
1908—January ..	0'13	30'25	3'16	0'156	0'059	0'149	0'364	0'260
February ..	0'96	35'25	4'48	0'098	0'053	0'106	0'257	0'261
Total for 12 months	24'05	133'00	37'35					4'323

(a) Only one analysis was made this month, the work being interrupted by the making of necessary changes in the collecting apparatus.

TABLE II.—Average Nitrogen Content of Rain and Snow.

Precipitation.	Number of samples.	Precipitation in inches.	Nitrogen (parts per million).				Nitrogen (percentage of total).		
			In free ammonia.	In albumenoid ammonia.	In nitrates and nitrites.	Total.	In free ammonia.	In albumenoid ammonia.	In nitrates and nitrites.
Rain	46	24'05	0'396	0'114	0'142	0'652	61	17	22
Snow	32	133'00	0'216	0'038	0'132	0'386	56	10	34

TABLE III.

	June 26 (morning).	June 26 (evening).
Precipitation, inches	0'05	0'16
Nitrogen, parts per million—		
As free ammonia	0'640	0'225
As albumenoid ammonia ..	0'205	0'105
As nitrates and nitrites ..	0'164	0'078

TABLE IV.

	July 24 (morning).	July 24 (evening).
Precipitation, inches	0'08	0'42
Nitrogen, parts per million—		
As free ammonia	0'330	0'230
As albumenoid ammonia ..	0'085	0'050
As nitrates and nitrites ..	—	—

compounds, the averages of the year show that in both rain and snow the proportion of nitrogen as free ammonia is the largest and that of the albumenoid ammonia (largely derived, no doubt, from dust, &c.), the smallest.

The richness of any specific fall of rain or snow in nitrogen compounds is largely influenced, no doubt, by the period that has elapsed since the previous precipitation, though the amount of rain or snow falling, naturally, determines to some degree the composition in this regard. One or two examples to illustrate these points may be taken from the year's record. Between the 18th and 26th of June there had been no rain. On the morning of the 26th 0'05 inch of rain fell, and again in the evening of the same day, 0'16 inch. The analytical data are given in Table III.

Again in July, after a period of three days without rain, similar results were obtained (Table IV.).

From the smaller percentage of nitrogen compounds in snow, to which we have already referred, it might be conjectured that the solvent or absorbent action of snow was less than that of rain, and this appears to be the case. Thus, snow fell to a depth of 8'75 inches during the early hours of December 30th, which on analysis was found to contain 0'09 p.p.m. nitrogen as free ammonia, 0'086 p.p.m. as albumenoid ammonia, and 0'115 p.p.m. as nitrates and nitrites, a total of 0'291 p.p.m. of snow-water. Later in the day, about 10.30 a.m., the temperature rose slightly and the snow turned to a light rain, of which a precipitation of 0'15 inch was recorded. Upon analysis this rain water gave 0'238, 0'271, and 0'582 p.p.m. of nitrogen in the form of the compounds mentioned, making a total of 1'101 p.p.m.

The rain and the snow, as we have seen, by their cleansing action upon the atmosphere furnish our soils

annually with a notable amount of that important constituent of plant food, nitrogen, in a form extremely available for crop use. It is important, however, to point out that while our data support the widely accepted view that snow is a direct fertiliser, it is very evident that its value in this respect has been considerably over-estimated by many of our farmers.—*Transactions of the Royal Society of Canada*, 1909, [3], ii., p. 181.

THE COMPLEXITY OF TELLURIUM.

By PHILIP E. BROWNING and WILLIAM R. FLINT.

ALTHOUGH the consensus of opinion among chemists at present seems to favour the homogeneity of tellurium (Köthner *Ann.*, cccxix., 1; Gutbier, *Sitzungsber. Phys.-med. Soc. Erlangen*, xxxvii., 270; Lenher, *Journ. Am. Chem. Soc.*, xxx., 387), and an atomic weight of 127'5, the recent work of Marckwald (*Ber.*, xl., 4730), and the last report of the International Committee on Atomic Weights (*Journ. Am. Chem. Soc.*, xxxi., 1) seem to suggest that possibly the question of the atomic weight at least has not been definitely settled.

The work described in this paper was suggested by the observation that when water is added in large amount to a solution of tellurium tetrachloride, this compound is hydrolysed and the greater part of the tellurous acid is precipitated, while some of the tellurium remains in solution however large the amount of water present.

This observation was apparently first made by Berzelius (*Ann. Chim. Phys.*, [11.], lviii., 113), and later the method applied in a limited degree by Brauner (*Journ. Chem. Soc.*,

lv., 382), and by Baker and Bennett (*Ibid.*, xci., p. 1849), to a process of fractionation.

It was further observed by us that the tellurium remaining in solution after the treatment with water and filtering may be completely precipitated as the dioxide by heating to boiling, treating first with ammonia and then with acetic acid in faint excess, as described in a previous paper from the Kent Chemical Laboratory, Yale University (*Am. Journ. Sci.*, xxviii., 112).

This procedure was applied with the result to be described, in order to determine whether by means of it any light might be obtained upon the possible complexity of tellurium.

About 100 grms. of crude tellurium, which had been extracted by hydrochloric acid from electrolytic copper residues, were subjected to a series of purification processes such as have been commonly used for the purpose of preparing pure material. This crude preparation was first twice fractionally precipitated by sulphur dioxide; then fused in portions in hydrogen with potassium cyanide, extracted with water, and precipitated from solution by a current of air. It was next re-precipitated by sulphur dioxide from hydrochloric acid solution; was fused in hydrogen, and finally distilled in a current of hydrogen from porcelain boats in a porcelain tube.

Ninety-two grms. of this pure product were converted to tetrachloride, and the solution, in as small amount of hydrochloric acid as possible, was diluted with 4 litres of boiling distilled water, and cooled. The precipitate, 76 grms. of pure white crystalline TeO_2 , was removed, and the filtrate was heated again to boiling, after which ammonia and then acetic acid in the smallest possible excess were added. When cold, 38 grms. of TeO_2 were obtained, more finely crystalline than the preceding fraction, but also pure white. The filtrate from this fraction contained no tellurium detectable by stannous chloride, and was consequently discarded.

These two fractions were next separately refractionated by an exact repetition of the process above described, each fraction secured being likewise refractionated, the three fractionations thus providing eight fractions, of which the last, about 1.5 grm., was set aside. Fraction 2 was combined with 3, 4 with 5, and 6 with 7, and each portion of the material refractionated, as was also Fraction 1. From this point on, the fractionation was carried out after the usual plan of fractional crystallisations, intermediate fractions being combined before re-treatment, and those at the latter end of the series being removed when small in amount (from 1 to 2 grms.). In this manner ten fractionations were performed, as a result of which were secured about 59 grms. of dioxide from the first, or water end, and 15 grms. from the last, or ammonia acetic end, of the series. Each of these portions was refractionated once, the water fraction (50 grms.) of the first being denominated α , and the ammonia acetic acid fraction (13 grms.) of the latter, β . The α - and β -fractions were lastly converted to

basic nitrate, the former by one and the latter by two crystallisations, according to the method described by Norris, Fay, and Ederly (*Am. Chem. Journ.*, xxiii., 105). It is to be noted that in the process of fractionation the material of each fraction had been crystallised out of a large amount of distilled water.

The α - and β -fractions were subjected to analysis by three different methods:—(1) The basic nitrate method; (2) the Gooch and Danner modification of Brauner's permanganate process (*Am. Journ. Sci.*, xlv., 301); and (3) the ammonia acetic acid method previously described.

1. After bringing the basic nitrate to constant weight at 140° as recommended by Norris (*Journ. Am. Chem. Soc.*, xxviii., 1675), carefully weighed portions were heated in platinum with a gradually increasing temperature for a period of five to six hours. The crucibles were contained in porcelain radiators, a porcelain dish being supported above each in an inverted position to distribute the heat more evenly. Finally, they were removed and ignited for a short time at dull redness until the dioxide had fused to a glassy condition. The weighings were conducted with properly standardised weights by the method of vibrations, and the usual corrections were applied. The results are recorded in Table I.

TALBE I.

Alpha.	2TeO ₂ .HNO ₃ taken.	TeO ₂ found.	TeO ₂ found.
	Grm.	Grm.	Per cent.
1.	0.09575	0.07986	83.40
2.	0.27354	0.22813	83.39
3.	0.60237	0.50272	83.45
4.	0.66288	0.55331	83.45
5.	1.60542	1.33912	83.41
6.	1.78565	1.48982	83.43
Beta.			
1.	0.08473	0.07081	83.57
2.	0.23125	0.19256	83.63
3.	0.87484	0.73306	83.79
4.	0.39778	0.33232	83.56
5.	0.39479	0.33005	83.60

The mean percentage of dioxide in α (83.42 per cent) gives an atomic weight of 126.53, that for β (83.63 per cent) 128.97. It is thus apparent that the fractions are not homogeneous with each other, since they had been crystallised under precisely similar conditions, with due precautions to secure constancy of composition in each case, and with exactly similar treatment in the performance of the analyses.

2. Analyses made by the permanganate process mentioned above confirm this difference. The material was dissolved with 2 cc. of 10 per cent potassium hydroxide, and the solution was acidified with sulphuric acid (1:1), 1 cc. in excess diluted to 100 cc. with water, and treated with an excess of permanganate, oxalic acid being then added in excess. The mixture was then warmed nearly to

TABLE II.

Alpha.	2TeO ₂ .HNO ₃ .	TeO ₂ theory.	TeO ₂ found.	Error on TeO ₂ .	Beta.	2TeO ₂ .HNO ₃ .	TeO ₂ theory.	TeO ₂ found.	Error on TeO ₂ .
	Grm.	Grm.	Grm.	Grm.		Grm.	Grm.	Grm.	Grm.
Te = 126.5.					Te = 127.5.				
1.	0.2537	0.2116	0.2119	+0.0003	1.	0.2504	0.2094	0.2095	+0.0001
2.	0.2508	0.2092	0.2093	+0.0001	2.	0.2500	0.2090	0.2086	-0.0004
3.	0.2521	0.2103	0.2102	-0.0001	3.	0.2505	0.2095	0.2095	—
4.	0.2508	0.2092	0.2092	—	4.	0.2505	0.2095	0.2095	—
5.	0.2523	0.2104	0.2100	-0.0004	5.	0.2504	0.2094	0.2100	+0.0006
6.	0.2511	0.2094	0.2092	-0.0002	6.	0.2501	0.2091	0.2093	+0.0002
Te = 128.9.					Te = 127.5.				
1.	0.2504	0.2094	0.2095	+0.0001	1.	0.2504	0.2094	0.2095	+0.0001
2.	0.2500	0.2090	0.2086	-0.0004	2.	0.2500	0.2090	0.2086	-0.0004
3.	0.2505	0.2095	0.2095	—	3.	0.2505	0.2095	0.2095	—
4.	0.2505	0.2095	0.2095	—	4.	0.2505	0.2095	0.2095	—
5.	0.2504	0.2094	0.2100	+0.0006	5.	0.2504	0.2094	0.2100	+0.0006
6.	0.2501	0.2091	0.2093	+0.0002	6.	0.2501	0.2091	0.2093	+0.0002

boiling, and the excess of oxalic acid determined by permanganate. The titrations were conducted in porcelain dishes. The results are given in Table II.

Computation from the permanganate required for the oxidation in each case, gave a mean of 126.64 for α , and 128.77 for β .

3. A similar difference was again obtained by the ammonia acetic acid process already referred to. The basic nitrate was dissolved with 2 cc. of hydrochloric acid, the excess of acid removed as much as possible by careful evaporation; the dilution was with 200 cc. of boiling distilled water, and the ammonia and acetic acid were added from burettes. Filtration was performed after standing over-night. These results appear in Table III.

TABLE III.

Alpha.	$2\text{TeO}_3 \cdot \text{HNO}_3$.	TeO_3	TeO_2	Error.	TeO_2 .
	Grm.	theory.	found		
		Grm.	Grm.	Grm.	Per cent
	(Te = 126.5).				
1.	0.2506	0.2090	0.2093	+0.0003	83.51
2.	0.2505	0.2089	0.2088	-0.0001	83.35
3.	0.2529	0.2109	0.2108	-0.0001	83.35
4.	0.2510	0.2094	0.2093	-0.0001	83.39
5.	0.2507	0.2091	0.2091	—	83.41
Beta.	(Te = 128.9).				
1.	0.2512	0.2101	0.2097	-0.0004	83.48
2.	0.2514	0.2102	0.2103	+0.0001	83.65
3.	0.2504	0.2094	0.2095	+0.0001	83.66
4.	0.2507	0.2096	0.2095	-0.0001	83.57
5.	0.2612	0.2101	0.2100	0.0001	83.60

For α the mean percentage of dioxide is 83.40 per cent, or Te = 126.31; β , 83.59 per cent, or Te = 128.81.

Summary of Analyses.

Process.	Alpha.	Beta.
Basic nitrate	126.53	128.97
Permanganate	126.64	128.77
Ammonia acetic acid ..	126.31	128.81
Mean	126.49	128.85

It is seen that an atomic weight of 126.5 gives more satisfactory results for α , while neither 126.5 nor 127.5 will answer for β .

Besides the experiments with the basic nitrate just described, the following experiments upon the dioxide are to be noted:—Two portions of tellurium dioxide from each fraction, prepared by the ignition of the basic nitrates, were dissolved in equal amounts of hydrochloric acid, and treated with equal amounts of boiling distilled water. The results given in Table IV. indicate different degrees of hydrolytic susceptibility on the part of the tetrachloride prepared from these fractions.

TABLE IV.

	TeO_2 taken.		TeO_2 found.		Percentage precipitated.
	Grm.	Grm.	Grm.	Grm.	
1.	0.3000	0.2521	0.2521	84.0	
2.	0.3000	0.2602	0.2602	86.7	
3.	0.3000	0.2772	0.2772	92.4	
4.	0.3000	0.2806	0.2806	93.5	

1 and 2 were obtained from one fraction, and 3 and 4 from the other. 1 and 3 stood twenty-two hours before filtration, 2 twenty-six hours, and 4 eighteen hours.

A sample of tellurium dioxide obtained from the tellurium tetrachloride by several hot water precipitations, according to the procedure for the preparation of the α fraction, was analysed by the permanganate process already described. The results of the analysis of this specially prepared dioxide, as given in Table V., show a close agreement with the analyses of the basic nitrate prepared from the α -fraction and recorded in Table II.

TABLE V.

	TeO ₂ (Te = 126.5).			TeO ₂ (Te = 127.5).	
	Taken. Grm.	Found. Grm.	Error. Grm.	Found. Grm.	Error Grm.
1.	0.3066	0.3064	- 0.0002	0.3076	+ 0.0010
2.	0.2723	0.2719	- 0.0004	0.2729	+ 0.0006
3.	0.2229	0.2228	- 0.0001	0.2243	+ 0.0014
4.	0.2220	0.2220	—	0.2235	+ 0.0015

It consequently appears from the analyses by three different methods that, in the end fractions obtained by fractional hydrolysis of tellurium tetrachloride prepared from the carefully purified element, tellurium seems to possess different atomic weights. It is not claimed that these atomic weights have been determined with the utmost accuracy. The two fractions, however, have been in each case treated exactly alike, in a manner entirely competent to show at least approximately whatever difference there might be. The preparations have been carefully examined to discover the presence of any impurities which might cause the difference, but no such impurities have been found. At present, therefore, there seems to be no explanation of the differences found other than the complexity of the original substance. The investigations just described are of necessity preliminary in character, and the results of a more extended study of this fractionation process, already begun by the latter of the two collaborators, will be published as soon as practicable.—*American Journal of Science*, xxviii., p. 347.

THE GRAVIMETRIC DETERMINATION OF FREE IODINE BY THE ACTION OF METALLIC SILVER.

By F. A. GOOCH and CLAUDE C. PERKINS.

WHEN in analytical operations it becomes desirable to determine free iodine in the presence of iodine combined in an iodide, it is usual to have recourse to volumetric procedure involving the preparation of standard sodium thiosulphate, for use in neutral or acid solution, or of standard arsenite, for use in solutions made alkaline by a bicarbonate.

The present paper is an account of an endeavour to utilise the well-known affinity between silver and iodine as the basis of a gravimetric method for the determination of iodine in general, and, incidentally, for the gravimetric standardisation of iodine solutions to be used in volumetric analysis.

Inasmuch as the facility with which combinations may take place between substances varies with their physical conditions, several preparations of silver were tried with a view to finding the form of silver best adapted to the purpose of taking up iodine in analysis. The iodine was used in N/10 solution prepared in the usual way (12.7 grms. of iodine to 18 grms. of potassium iodide in one litre) and standardised against arsenious acid.

The procedure was simple. The standard N/10 iodine solution was drawn from a burette into a 250 cc. Erlenmeyer flask containing a weighed amount of finely divided silver. The flask, properly trapped and attached to a mechanical shaker adjusted to give the liquid a rapid rotary motion, was shaken until the iodine colour had vanished. The liquid, usually 50 cc. in volume, was diluted to about 100 cc., and the residue of silver and silver iodide, collected in a perforated crucible fitted with asbestos felt, was washed, dried at 130° to 140°, and weighed. The difference between the weight of silver taken and that of the residue of silver and silver iodide should, according to the theory of action, be the measure of the free iodine. A cut in original shows the mechanical shaker and the adjustment of apparatus used throughout the work. A flask at one side, fitted with

a bulb-trap held in place by an outer rubber band, was used in the experiments of Tables I. and II. A flask mounted upon the shaker was used for the operations carried out in hydrogen and recorded in Tables III. and IV.

In Table I. are given the results of experiments made with silver reduced in the wet way, by the action of zinc upon silver chloride (A), silver nitrate (B), or silver iodide (C); and, in a dry way, by the action of hydrogen upon silver sulphide (D), or upon silver oxide (E). In the first set of experiments of each sort the reduced silver was dried and used without special previous treatment; in the second set of each sort the reduced silver was shaken with a solution of potassium iodide, washed, and dried before being used to absorb the iodine. The object of shaking the reduced silver with potassium iodide was to convert to silver iodide any incompletely reduced silver chloride, nitrate, or sulphide, and this treatment does reduce considerably the very large error noted in all of the experiments with the untreated silver; but the similar, if less marked, effect upon silver reduced from the iodide suggested that a part of the unfavourable effects in the case of the untreated silver might be due to action between potassium iodide and metallic components of the zinc. Even in those experiments in which the reduced silver was previously treated with potassium iodide the errors are too large and too variable for a good analytical process.

TABLE I.—The Action of Silver Reduced by Chemical Processes.

Silver taken. Grms.	Iodine taken. Grm.	Increase in weight of silver. Grm.	Error in iodine. Grm.
A.—The Action of Silver reduced from AgCl by Zinc.			
3	0.6473	0.6833	+0.0360
3	0.6473	0.6861	+0.0388
3	0.6473	0.6877	+0.0404
3	0.6473	0.6830	+0.0357
3	0.6473	0.6829	+0.0356
3	0.6461	0.6475	+0.0014
3	0.6461	0.6483	+0.0022
3	0.6461	0.6494	+0.0033
B.—The Action of Silver reduced from AgNO ₃ by Zinc.			
3	0.6461	0.6677	+0.0216
3	0.6461	0.6656	+0.0195
3	0.6461	0.6464	+0.0003
3	0.6461	0.6472	+0.0011
3	0.6461	0.6470	+0.0009
C.—The Action of Silver reduced from AgI by Zinc.			
3	0.6461	0.6513	+0.0052
3.27	0.6461	0.6519	+0.0058
3	0.6461	0.6514	+0.0053
3	0.3217	0.3257	+0.0040
3	0.3217	0.3261	+0.0044
3	0.6434	0.6444	+0.0010
3	0.3217	0.3231	+0.0014
D.—The Action of Silver reduced from Ag ₂ S by Hydrogen.			
3	0.6473	0.6574	+0.0101
3	0.6473	0.6577	+0.0104
3.002	0.6461	0.6473	+0.0012
3	0.6461	0.6472	+0.0011
3	0.6461	0.6475	+0.0014
3	0.6461	0.6483	+0.0022
3	0.6461	0.6525	+0.0064
E.—The Action of Silver reduced from Ag ₂ O by Hydrogen.			
3	0.3217	0.3250	+0.0033

(a) The silver was used without previous treatment.

(b) The silver was previously treated with KI.

(c) Stood for several hours in the solution.

The experiments next described were made with silver deposited electrolytically from a solution of silver nitrate upon a platinum cathode, the anode being enclosed within a porous cell to prevent admixture of the silver dioxide formed at the anode with the metallic silver at the cathode. Experience showed that while the bright and crystalline deposit which formed upon a stationary cathode lacked in absorptive power, the product obtained by continually oscillating the cathode during the deposition of the metal, broken and dark when formed, proved to be sensitive to iodine as well as pure. The results of experiments with electrolytic silver thus prepared are given in Table II.

TABLE II.—The Action of Electrolytic Silver.

Silver taken. Grms.	Iodine taken. Grm.	Increase in weight of silver. Grm.	Error in iodine. Grm.
2.8184	0.6461	0.6494	+0.0033
3.2130	0.6461	0.6490	+0.0029
2.0514	0.6461	0.6491	+0.0030
3.0102	0.6461	0.6490	+0.0029
7.5943 (cryst.)	0.6479	0.6513	+0.0034

Though the silver used in this process was pure, the errors observed are positive and high; and this fact emphasises an obvious inference from the previous work that the excess in weight is due to the absorption by the silver of an extra amount of iodine liberated from the potassium iodide by prolonged agitation in contact with the air. In harmony with this idea is the fact, observed throughout the entire series of experiments with silver reduced by chemical processes and subsequently treated with potassium iodide, that the error is greatest when the time used to accomplish the absorption is the longest. This was especially marked in the experiments with silver reduced by hydrogen, in which the largest amount of time was needed, on account of the less sensitive character of the glistening and filamentary metal.

Moreover, direct experiments in which the silver was shaken with 50 cc. of a solution of potassium iodide, 20 grms. to the litre, fully confirmed the idea that the action of air must be prevented during the agitation of the solution of the iodide in contact with silver; for in these experiments it was found, that from the solution of potassium iodide shaken in contact with air, finely divided electrolytic silver absorbed 0.0010 gm. of iodine in fifteen minutes, that silver reduced by zinc from silver iodide absorbed 0.0012 gm. of iodine in fifteen minutes, that silver reduced from the sulphide by hydrogen took up 0.0032 gm. of iodine in one hour, and that crystalline electrolytic silver took up 0.0051 gm. in one hour and forty-five minutes.

This action of air once shown, the next step was to investigate the behaviour of silver in contact with potassium iodide protected from the action of the air. In Table III. are recorded the details of experiments in which the standard N/10 solution of iodine in potassium iodide was shaken with N/10 silver in flask filled with hydrogen and closed.

These results make it plain that free iodine may be determined with accuracy in the presence of potassium iodide by shaking the solution with metallic silver in a closed flask filled with hydrogen and determining the increase in weight of the silver. Silver reduced from a silver salt by zinc or from silver sulphide by hydrogen may serve the purpose, provided it is subjected to a preliminary treatment with potassium iodide, and silver reduced from the oxide by hydrogen is also serviceable; but the best form of silver, and the one most easily prepared in the pure state, is that deposited electrolytically upon a small oscillating cathode of platinum from a solution of silver nitrate, the platinum anode being enclosed in a porous cell. The shaking of the silver may be done by hand or by some simple form of mechanical shaker like that described in the figure. The time required for the absorption of approximately 0.65 gm. of iodine in 50 cc. of liquid was fifteen to twenty-five minutes. The mean error of the

eleven determinations in which electrolytic silver was employed proved to be -0.0001 grm. between extremes of $+0.0005$ and -0.0004 grm.

TABLE III.—*The Action of Silver upon N/10 Iodine in an Atmosphere of Hydrogen*

Silver taken. Grms.	Iodine taken. Grm.	Increase in weight of iodine. Grm.	Error in iodine. Grm.
A.—The Action of Silver reduced from AgCl by Zinc and treated with KI.			
3.0000	0.6461	0.6464	$+0.0003$
1.0000	0.6447	0.6448	$+0.0001$
Average			$+0.0002$

B.—The Action of Silver reduced from AgI by Zinc and treated with KI.

3.6293	0.3217	0.3221	$+0.0004$
3.2049	0.3217	0.3225	$+0.0008$
3.0000	0.3217	0.3219	$+0.0002$
3.0068	0.3217	0.3212	-0.0005
3.0049	0.3217	0.3221	$+0.0004$
3.0026	0.6434	0.6441	$+0.0007$
2.9990	0.3217	0.3214	-0.0003
3.0005	0.3217	0.3214	-0.0003
Average			$+0.0002$

C.—The Action of Silver reduced from Ag₂S by Hydrogen and treated with KI.

3.0000	0.6461	0.6463	$+0.0002$
3.0000	0.6461	0.6460	-0.0001
Average			$+0.0001$

D.—The Action of Silver reduced from Ag₂O by Hydrogen.

3.0000	0.6434	0.6443	$+0.0009$
3.0000	0.6434	0.6430	-0.0004
Average			$+0.0003$

E.—The Action of Silver reduced Electrolytically from AgNO₃.

4.4189	0.6447	0.6447	± 0.0000
3.0025	0.6447	0.6448	$+0.0001$
3.0009	0.6447	0.6443	-0.0004
3.0157	0.6447	0.6445	-0.0002
3.0000	0.6447	0.6444	-0.0003
3.0000	0.6447	0.6452	$+0.0005$
3.0004	0.6447	0.6443	-0.0004
3.0043	0.6447	0.6443	-0.0004
3.0000	0.6434	0.6430	-0.0004
3.5810	0.3217	0.3221	$+0.0004$
3.0000	0.3217	0.3219	$+0.0002$
Average			-0.0001

To test the accuracy of the process in alkaline solution experiments similar to those above were made, in which the mixture of silver and iodine was made alkaline by adding about 10 cc. of a saturated solution of sodium bicarbonate. The results of the experiments in Table IV., which show irregularities when made in air and a very high degree of accuracy when the shaking was done under hydrogen, prove the absorption of iodine to be equally as exact in the alkaline as the neutral solution.

The process described, in which free iodine is absorbed by electrolytic silver under hydrogen, either in neutral solution or in a solution made alkaline with an acid carbonate, should be applicable in many analytical operations, as well

TABLE IV.—*The Action of Silver upon N/10 Iodine in an Alkaline Solution.*

Silver taken. Grms.	Iodine taken. Grm.	Increase in weight of silver. Grm.	Error in iodine. Grm.
A.—The Action of Silver shaken in Air with NaHCO ₃ .			
2.0110	0.3217	0.3221	$+0.0004$
3.6684	0.3217	0.3219	$+0.0002$
3.0056	0.3217	0.3235	$+0.0018$
3.0093	0.3217	0.3245	$+0.0028$
3.0058	0.3217	0.3224	$+0.0007$
3.6686	0.3217	0.3243	$+0.0026$
2.9993	0.3217	0.3261	$+0.0044$
3.0013	0.3217	0.3235	$+0.0018$
3.0014	0.6434	0.6485	$+0.0051$
Average			$+0.0022$

B.—The Action of Silver shaken in an Atmosphere of Hydrogen with NaHCO₃.

3.0014	0.3217	0.3216	-0.0001
3.0169	0.3217	0.3216	-0.0001
3.0083	0.6434	0.6433	-0.0001
3.0016	0.2500	0.2503	$+0.0003$
3.0069	0.3217	0.3219	$+0.0002$
Average			$+0.0001$

as in the gravimetric standardisation of the usual iodine solution of volumetric analysis.—*American Journal of Science*, xxviii., p. 33.

A REVISION OF THE ATOMIC WEIGHTS OF IODINE AND SILVER.*

(PRELIMINARY PAPER).

By GREGORY PAUL BAXTER and GEO. STEPHEN TILLEY.

(Concluded from p. 286).

THE atomic weights of iodine and silver calculated from the ratio of silver to pentoxide depend of course upon the ratio of the atomic weights of silver and iodine. The latter ratio has recently been subjected to careful revision by one of us (Baxter, *Proc. Am. Acad.*, 1905, xli., 73), and has been found to have the value 0.848843. Using this ratio the atomic weight of silver calculated from the above data is 107.847.

This value is highly sensitive to changes in the ratio of silver to iodine, a negative error of one one-hundredth of a per cent producing a negative error of three-hundredths of a per cent in the atomic weight of silver. Hence if the above value of the atomic weight of silver is too low, it might be expected that the ratio of silver to iodine also is too low. From the work of both Köthner and Aeuer (*Liebig's Ann.*, 1904, cccxxvii., 123), and Baxter, however, it seems certain that the ratio of silver to iodine is at any rate no higher than the value used in our calculations.

The result of the experiments which have been described is unexpected. For although several recent investigations have shown that the atomic weight of silver may be possibly as low as 107.87, referred to oxygen 16.000, no evidence has yet been published which indicated a value as low as the foregoing. Accordingly, a new series of experiments was undertaken, similar to the early one, with even greater pains to avoid possible sources of error.

Two new specimens of iodic acid were prepared. In order to determine whether crystallisation of the iodic acid alone was sufficient purification, Sample II. was made from iodine which had been purified by only a single distillation from solution in an iodide, and then by one from water,

* Contribution from the Chemical Laboratory of Harvard College. From the *Journal of the American Chemical Society*, xxi., No. 2.

THE RATIO OF SILVER TO IODINE PENTOXIDE.

Series I.—By G. S. TILLEY.

(Sample I. of Iodic Acid and Sample B of Silver were used).

No. of analysis.	Corrected weight of I_2O_5 in vacuum.	Weight of Ag in vacuum.	Weight of AgI.	Corrected weight of Ag in vacuum.	Ratio, 2Ag : I_2O_5 .
	Grms.	Grms.	Grm.	Grms.	
(a) 1.	6.06570	3.92046	0.00042	3.92027	0.646234
2.	9.48035	6.12703	0.00200	6.12611	0.646223
3.	7.73052	4.99599	0.00077	4.99564	0.646231
4.	12.63909	8.16804	0.00058	8.16777	0.646208
5.	9.49913	6.13884	0.00094	6.13841	0.646239
6.	8.34369	5.39206	0.00008	5.39202	0.646216
7.	8.83155	5.70748	0.00071	5.70715	0.636216
	6.77487	4.37836	0.00071	4.37803	
Average					0.646225

Series II.—By G. P. BAXTER.

No. of analysis.	Sample of I_2O_5 .	Sample of Ag.	Corrected weight of I_2O_5 in vacuum.	Weight of Ag in vacuum.	Weight of AgI from filtrate.	Corrected weight of Ag in vacuum.	Ratio, 2Ag : I_2O_5 .
			Grms.	Grms.	Grm.	Grms.	
8.	II.	B	12.09036	7.81397	0.00167	7.81320	0.646234
9.	II.	B + C	6.29744	4.07015	0.00127	4.06957	0.646226
10.	II.	A	10.89880	7.04362	0.00092 (b)	7.04309	0.646226
11.	II.	D	9.33895	6.03554	0.00106	6.03505	0.646222
12.	II.	A	10.15370	6.56194	0.00055	6.56160	0.646236
13.	III.	D	11.00453	7.11201	0.00130	7.11141	0.646226
14.	III.	A	7.01649	4.53456	0.00055	4.53431	0.646236
15.	III.	D	9.33573	6.03362	0.00125	6.03304	0.646231
16.	III.	D	8.72163	5.63666	0.00103	5.63619	0.646231
17.	III.	D	9.01524	5.82603	0.00025	5.82591	0.646229
Average							0.646230

(a) The first two analyses were inadvertently mixed, and hence are combined in the table.

(b) AgBr.

while the nitric acid was once distilled through a quartz condenser with no special attempt to remove chlorine. A portion of the iodic acid was prepared in the transparent fused quartz flask as already described. The remainder was made in a large opaque fused-quartz dish nearly 1 litre in capacity. The inside of this dish had been abraded with sand to break the edges of the bubbles, and had been digested for hours with acid solutions to remove soluble impurities. The combined specimens of acid were crystallised at least ten times in dishes of transparent fused quartz, with centrifugal drainage, until free from the organic odour previously mentioned. In the preparation of this sample the solutions were always heated and evaporated upon an electric stove under a large Victor Meyer funnel, instead of in the special evaporating apparatus previously described.

The second specimen of acid was prepared from iodine resulting from the decomposition of the iodine pentoxide in the water determinations. It was first dissolved in pure sulphurous acid and then set free from solution by distillation with re-crystallised potassium permanganate, a little less permanganate than was necessary to set free all the iodine being employed. The product was thus distilled once from a dilute solution of an iodide. Finally, the iodine was once distilled from pure water. The nitric acid for this preparation was carefully freed from chlorine by double distillation with a quartz condenser as previously described. The iodine was converted into iodic acid by treatment with the nitric acid in the large opaque quartz dish used for the preparation of Sample II. Before the crystallisation of the iodic acid was commenced, the powder resulting from the treatment of the iodine with nitric acid was drained and heated on the electric stove until apparently all nitric acid had been expelled. Then it was heated to 300° in a current of pure dry air in small portions in a platinum boat. The resulting iodine pentoxide was dissolved in water, and at least ten times re-crystallised in quartz dishes from solution in the purest water, with centrifugal drainage in platinum Gooch crucibles. In spite

of the drastic treatment to which the iodine had been subjected before conversion into iodic acid, the mother-liquors of the first crystallisation were by no means free from the organic odour previously observed, although nitric acid seemed to have been completely removed. This odour disappeared gradually during crystallisation as before, and the final product was free from odour. This specimen is designated Sample III.

Two new specimens of silver were employed. A portion of one had already been used in an investigation upon the atomic weight of lead (Baxter and Wilson, *Proc. Am. Acad.*, 1907, xliii., 365). This sample was precipitated once as silver chloride, once as metal by ammonium formate, and was finally electrolysed. This specimen is designated Sample C. Sample D was employed in an investigation upon the atomic weight of bromine (Baxter, *Proc. Am. Acad.*, 1906, xlii., 201). It was first purified in part by precipitation as chloride, in part by precipitation with ammonium formate. The combined material was then subjected to two electrolyses. Both specimens were finally fused in a current of pure hydrogen.

The acid was converted into pentoxide exactly as in the first series. Then, after weighing, it was dissolved and reduced with a slight excess of hydrazine as before, and precipitated with a slight excess of silver. After filtration and evaporation of the filtrate the excess of silver was determined gravimetrically as silver iodide in a Gooch-Munroe-Naubauer crucible.

Essentially no change was made in the method of analysis in Analyses 8 and 9 except that a slight excess of hydrazine was employed. At this point a tube 50 cm. in length filled with glass pearls was substituted for the column of bulbs in the reduction apparatus, since it was feared that traces of the spray produced by the effervescence during reduction might have been carried through the bulbs by the current of nitrogen disengaged. The pearls were moistened with sulphurous acid before reduction was commenced. This change in the apparatus was without

effect, the succeeding five analyses giving results identical with previous ones. In Analyses 15 to 17 the method of precipitation was reversed by pouring the iodide solution into the silver nitrate solution. This change also was without effect, hence it is reasonably certain that the dilution of the solutions during precipitation was sufficient to prevent occlusion of perceptible amounts of either iodide or silver nitrate. It is worth pointing out that occlusion of iodide would lower the observed atomic weight of silver, while occlusion of silver nitrate would produce the opposite effect. The occlusion of ammonium nitrate by the silver iodide would, of course, be without influence upon the final result.

In one analysis which is not recorded in the table about one-quarter of the iodic acid was reduced by means of sulphurous acid, the ratio of silver to iodine in this experiment being slightly higher than in the other cases, owing doubtless to the occlusion of silver sulphate. In another analysis the attempt was made to precipitate the silver iodide from ammoniacal solution by adding the silver nitrate solution to the slightly ammoniacal solution of the iodide. Köthner and Aeuer (*loc. cit.*), and Baxter have shown that silver iodide formed in ammoniacal solution is freer from occluded matter than when formed in acid solution. This experiment was a failure, for silver was reduced to the metallic state owing to the slight excess of hydrazine.

The question of adsorption of silver nitrate by the precipitate was further tested in several instances by evaporating the wash-waters of the silver iodide separately from the filtrate. In every such case only a mere trace of silver could be detected, even when the precipitate was allowed to stand in contact with the wash-waters for several hours.

No experiments were performed to test for complete reduction of the iodic acid to hydriodic acid, since evidence upon this point is already available. Sammet (*Zeit. Phys. Chem.*, 1905, liii., 640) has recently determined the equilibrium constant for the reaction of iodides upon iodates in acid solution to be as follows:—

$$\frac{(H^+)^6 \cdot (IO_3^-) \cdot (I^-)^5}{(I_2)^3} = 2.8 \cdot 10^{-47}.$$

i.e.,—

$$IO_3^- = \frac{(I_2)^3}{(H^+)^6 \cdot (I^-)^5} \cdot 2.8 \cdot 10^{-47}.$$

Since after reduction by the hydrazine the concentration of the free iodine approximates zero, and since the concentrations of the hydrogen and iodide ions are fairly large, and since the constant itself is extremely small, it is evident that the concentration of residual iodate must have been vanishingly small.

A few analyses which met with known accidents are omitted from Series II.

The average of Series II. is higher than Series I. by less than one one-thousandth of a per cent, the atomic weight of silver calculated from the ratio of silver to pentoxide being 107.850. While it is true that impurity in the iodic acid not containing halogens would tend to lower the observed atomic weight of silver, the close agreement of the two series carried out with material of fairly diverse nature practically eliminates impurity in the iodic acid or silver as the cause of the low resulting value for the atomic weight of silver. Sample I. of iodic acid was crystallised only three times from aqueous solution, while Samples II. and III. were both crystallised at least ten times. It is improbable that any impurity could have passed through the additional crystallisations without appreciable diminution in quantity. It has already been shown that mineral impurities were surely absent even before the crystallisation of the acid. Nitric acid could hardly have survived the prolonged heating at 240°, even if it had not been completely removed by the many crystallisations of the iodic acid.

With regard to impurities containing halogens other than iodine, it may be pointed out that Samples I. and III. were prepared from iodine and nitric acid which had been very thoroughly freed from chlorine and bromine, while even in the case of Sample II. only traces of chlorine could have been present. Aside from these facts it is decidedly improbable that an oxygen acid of either chlorine or bromine could have been formed and then have accompanied the iodic acid during its purification, for during the heating of the acid both before and after crystallisation such impurities would have been either volatilised or destroyed. Impurity of chlorine would probably tend to lower the observed atomic weight of silver on account of the relatively high solubility of silver chloride. For the same reason a trace of chlorine in either the hydrazine or the nitric acid employed in the analysis would have had no injurious effect. Impurity of bromine would produce the reverse effect if present in the form of a compound analogous to iodine pentoxide.

The presence of a halogen of higher atomic weight than iodine, forming an insoluble silver salt, if present as pentoxide would lower the observed atomic weight of silver. The existence of such an element is purely hypothetical, however, and what evidence exists is contrary to such an hypothesis. One of us has recently searched for such an element in vain (Baxter, *Proc. Am. Acad.*, 1904, xl., 422).

Two other possible contingencies must be considered, the presence of either free iodine or oxides of iodine higher than the pentoxide. Free iodine might result from reduction of the pentoxide during the heating. Such reduction or decomposition actually does take place to an extremely slight extent when the pentoxide is heated to 240°, for traces of free iodine can be detected in air that has been passed over iodine pentoxide at that temperature. That no appreciable quantity of iodine could remain in the pentoxide was shown by the fact that the solutions of the pentoxide were always absolutely colourless even when concentrated. Furthermore, it was found by experiment that a mere trace of iodine could be detected by its colour in such a solution. About one one-hundredth of a per cent of iodine in the pentoxide could be necessary to raise the observed atomic weight of silver by one one-hundredth of a unit.

Iodine heptoxide might result from either the presence of periodic acid in the iodic acid or from auto-oxidation of the pentoxide during the heating. Both possibilities are wanting in plausibility, for it is not at all probable in the light of the known instability of the heptoxide that the latter substance could have withstood the high temperature of heating. Twenty-five thousandths of a per cent of heptoxide in the iodic acid would be necessary to lower the observed atomic weight of silver by one one-hundredth of a unit.

Although it is intended to pursue the study of iodic acid farther in this laboratory, and the results presented in this paper are published subject to revision, it is of interest to consider the bearing of these results upon other recent investigations. Noyes and Weber have found the atomic weight of chlorine, referred to oxygen 16.000, to be 35.452 (*Journ. Am. Chem. Soc.*, 1908, xxx., 13; Morley's value for hydrogen is used). Assuming the ratio of silver to chlorine found by Richards and Wells, 3.04260, the atomic weight of silver calculated from Noyes and Weber's results is 107.866. On the other hand, Edgar (*CHEMICAL NEWS*, 1908, xcvi., 97) finds chlorine to be 35.461 referred to oxygen 16.000, whence silver is 107.893. Richards and Forbes have found the per cent of silver in silver nitrate to be 63.5005 (*Pub. Car. Inst.*, 1907, lxi., 47). Upon this basis, if the atomic weight of silver is assumed to be 107.850, the atomic weight of nitrogen is 13.991. The results of this research certainly confirm the belief that Stas's values for the atomic weights of silver and nitrogen are much too high.

We are very greatly indebted to the Carnegie Institution of Washington for pecuniary assistance which has done much to aid the progress of this research; also to the

Cyrus M. Warren Fund for Research in Harvard University for many indispensable platinum vessels.

The results of this research may be briefly summed up follows:—

1. The preparation of pure iodic acid is described.
2. The existence of the compound $I_2O_5 \cdot HIO_3$ is confirmed.
3. It is shown that while iodic acid may be almost completely converted to pentoxide by heating at 240° a small proportion of water remains, which is constant for definite conditions of heating.
4. It is shown that silver iodide occludes silver sulphate and that sulphur dioxide may not be used as a reducing agent if the iodine is to be precipitated by means of silver.
5. Hydrazine salts are found to be suitable reducing agents.
6. The specific gravity of iodine pentoxide at 25° referred to water at 4° is found to be 4.80.
7. It is shown that iodine pentoxide does not adsorb appreciable amounts of air.
8. The ratio of silver to iodine pentoxide is found to be 0.646230.
9. Upon this basis, if oxygen is assumed to be 16.000, the atomic weight of silver is 107.850 and that of iodine is 126.891.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, December 2nd, 1909.

Prof. HAROLD B. DIXON, F.R.S., President, in the Chair.

(Concluded from p. 301).

275. "The Correction of the Specific Gravity of Liquids for the Buoyancy of Air." By JOHN WADE and RICHARD WILLIAM MERRIMAN.

In determining the specific gravity of liquids to the fifth decimal place, neglect of variations in atmospheric density may lead to serious error, more especially when the water-content of the pycnometer is not determined under the same atmospheric conditions as those obtaining at the time of weighing the liquid. Analysis of the limits of accuracy of the customary correction formula leads to some simple expressions which, with the aid of tabulated constants, materially reduce the labour of correction.

276. "Syntheses with the Aid of Monochloromethyl Ether. Part II. The Action of Monochloromethyl Ether on the Sodium Derivative of Ethyl Acetoacetate." By JOHN LIONEL SIMONSEN and ROBERT STOREY.

The authors showed that monochloromethyl ether and ethyl sodioacetoacetate condense with the formation of ethyl methoxy- β -methoxycrotonate and ethyl α -diacetylglutarate.

277. "The Relation between the Chemical Constitution of Monazo-dyes and their Fastness to Light." By EDWIN ROY WATSON, A. CHANDRA SIKKAR, and JATINDRA M. DUTTA.

From rules which had already been formulated by one of the authors (*Proc. Chem. Soc.*, xxv., 224) it was expected that the dyes sulphobenzeneazophenolmonosulphonic acid and sulphobenzeneazophenoldisulphonic acid would be very fast to light. This was found to be the case. Sulphobenzeneazophenol was also found to be very fast to light. Contrary to the usual assumption that a hydroxy- or amino-group must be present in an azo-compound to give it dyeing properties, it was found that azobenzenedisulphonic acid is a dye, and, owing to the presence of sulphonic groups and the absence of any hydroxy- or amino-group, it was found to be very fast to light.

It was predicted that phenol would be formed as one of the decomposition products when chrysoidine faded in

light, and when this was put to the test phenol was found.

It was also predicted that the introduction of bromine atoms or a nitro-group into the phenolic or arylamino-part of a monazo-dye would increase its fastness to light, and that the fastness to light of aminoazobenzene would depend on the position of the amino-group, *m*-aminoazobenzene being faster than *p*-aminoazobenzene. The fastness to light of the following dyes was compared:—Aminoazobenzene, benzeneazodibromoaniline; benzeneazophenol, benzeneazonitrophenol; sulphobenzeneazophenol, sulphobenzeneazonitrophenol; *p*-aminoazobenzene, *m*-aminoazobenzene, and *o*-aminoazobenzene. The theory, on which these predictions were based, as to the manner of fading of azo-dyes in light was not confirmed by this investigation to the extent anticipated.

278. "The Triazo-group. Part X. Triazoantipyrene." By MARTIN ONSLOW FORSTER and ROBERT MÜLLER.

The preparation and properties of triazoantipyrene were described, and attention was drawn to the behaviour which distinguishes it from other triazo-ketones.

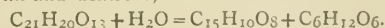
279. "Volumetric Estimation Sulphates." By ALEC DUNCAN MITCHELL and CLARENCE SMITH.

The method consists essentially of adding a small excess of 2N/5-barium chloride solution, destroying mineral acid by sodium acetate, adding excess of N/10-ammonium dichromate solution, and making up to 100 cc.; when the precipitate has settled, 25 cc. of the clear supernatant liquid are titrated with N/20 ferrous ammonium sulphate solution, using potassium ferricyanide as an external indicator.

This has been applied to ammonium sulphate, sodium sulphate, potassium sulphate, zinc sulphate, magnesium sulphate, and copper ammonium sulphate, and gives results accurate to about 0.2 per cent, although in the case of potassium sulphate special precautions have to be adopted to minimise adsorption. Excluding weighings, five determinations may easily be made in an hour.

280. "The Colouring Matter of Cotton Flowers. Gossypium herbaceum." (Part II.). By ARTHUR GEORGE PERKIN.

The flowers of the Egyptian cotton plant, a variety of the *Gossypium herbaceum*, have been found to contain three hitherto unknown glucosides. *Quercimeritrin*, $C_{21}H_{20}O_{12}$, the main constituent, crystallises with $3H_2O$ in small yellow plates, m. p. $247-249^\circ$, dyes mordanted fabrics very similarly to quercetin, and gives with lead acetate an orange-red precipitate. It forms an *octo-acetyl* compound, $C_{21}H_{12}O_{12}(C_2H_3O)_8$, colourless needles, m. p. $214-216^\circ$, and is hydrolysed with difficulty according to the equation $C_{21}H_{20}O_{12} + H_2O = C_{15}H_{10}O_7 + C_6H_{12}O_6$ into quercetin and dextrose (osazone, m. p. $204-205^\circ$). *isoQuercitrin*, $C_{21}H_{20}O_{12}$ (dried at 160°) consists of pale yellow needles, m. p. $217-219^\circ$, and is readily hydrolysed by acid, $C_{21}H_{20}O_{12} + H_2O = C_{15}H_{10}O_7 + C_6H_{12}O_6$, with formation of quercetin and dextrose, but differs from quercimeritrin in several important respects. With lead acetate it gives a bright yellow precipitate, dyes mordanted fabrics similarly to quercitrin (*Trans.*, 1902, lxxxi., 480), and is present in the flowers in small amount. The third glucoside, *gossypitrin*, $C_{21}H_{20}O_{13}$ (dried at 160°), pale orange-yellow needles, m. p. about $200-202^\circ$, when hydrolysed gives gossypetin and dextrose,—



It yields a bright red precipitate with lead acetate, and dyes mordanted fabrics. The flowers yielded 1.86 per cent of yellow colouring matter, consisting of quercetin mixed with about 10 per cent of gossypetin.

281. "Viscosity and Association in Binary Mixtures of Liquids." By GEORGE SENTER.

In a recent paper (*Trans.*, 1909, xcv., 1556) dealing with the viscosity of binary mixtures of liquids, Dunstan and Thole state that the maxima observed in certain viscosity-concentration curves of such systems "invariably occur at or near points of simple molecular composition," and

are connected with the formation of definite chemical compounds between the components of the mixture. In this connection they refer to the brief discussion of this subject in the author's "Outlines of Physical Chemistry" (p. 305), in which it is stated that no general agreement has yet been reached with reference to the interpretation of such curves, and they suggest that the considerations there advanced present no obstacle to the general acceptance of the association explanation of the phenomenon.

The experimental work described by Dunstan and Thole was undertaken with the object of throwing light on the displacement of the maxima with temperature, but, unfortunately, observations have only been made over a range of 10° ($20-30^{\circ}$), which is too small to allow of any very definite conclusion being drawn. However, it is known from the observations of Arrhenius, quoted in the paper, that in mixtures of ethyl alcohol and water, the viscosity maximum at 0° occurs at a composition of 36 per cent of alcohol, and at 55° at 50 per cent of alcohol, so that there is an undoubted shift of the maximum with temperature in this case, and doubtless in other cases.

Dunstan and Thole now maintain that such a shift of the maximum does not disprove the association explanation of this phenomenon, and with this the author agrees. It does, however, entirely disprove the suggestion that such maxima invariably occur "at" points of simple molecular composition, since the position of the maximum in the case cited alters continuously with rise of temperature through a wide range of concentration. The qualifying word "near" does not seem to have any well-defined meaning in the present case, as a mixture of two components in any proportions whatever may be looked upon as being "near" a point of simple molecular composition.

Even if the association explanation of the maxima be accepted, it is improbable that the observations throw any light on the composition of the compounds unless the latter are exceptionally stable, like $\text{H}_2\text{SO}_4(\text{H}_2\text{O}, \text{SO}_3)$ and $\text{H}_2\text{SO}_4, \text{H}_2\text{O}$. In this connection it is suggestive to note that, according to Kremann (*Monatsh.*, 1907, xxviii., 831), the viscosity curve of the system *m*-cresol-aniline, at 0° , shows a maximum at 85 mol. per cent of the former, although the components only form one compound, containing one molecule of each. Similarly, the viscosity curve of the system phenol-aniline shows a maximum at 67 mol. per cent of phenol, although only one compound is known containing the components in molecular proportions.

The numerous investigations on alloys carried out in recent years appear to throw some light on this question. According to Tamman (*Zeit. Anorg. Chem.*, 1907, liii., 446), it is a general rule that metals belonging to the same natural group form solid solutions (mixed crystals), but no chemical compounds. Now, Kurnakoff and Schemtschuschny (*Zeit. Anorg. Chem.*, 1908, lx., 1) have shown with reference to the hardness of binary systems (a property allied to viscosity)—(1) that the hardness of an unbroken series of solid solutions is often represented by a continuous curve showing a maximum; (2) that a chemical compound may be harder or softer than either of the components. It is not improbable that similar rules may apply to the viscosity of liquid mixtures. There does not seem to be any reason to assume *a priori* that the viscosity of a compound must be greater than that of its components, especially if the latter are themselves associated.

With reference to the two systems showing maxima specially dealt with in the paper by Dunstan and Thole, cited above, it may be noted that the freezing-point curve of mixtures of acetic acid and water shows no indications of the presence of a compound (Kremann, *Monatsh.*, 1907, xxviii., 893), although the observations were made at a lower temperature than the viscosity measurements described in the paper. Moreover, Jones (*Zeit. Phys. Chem.*, 1894, xiii., 419) has shown that mixtures of ethyl alcohol and water exert their effect on the freezing-point of acetic acid quite independently; he thus obtained no evidence of combination between the first two compounds,

although the corresponding experiments with mixtures of sulphuric acid and water showed quite conclusively the formation of compounds.

The fact that the maxima on the viscosity curves become less distinct the higher the temperature does not appear very conclusive from the point of view of association, as it is a rule of very wide applicability that the simple laws (in this case, the mixture law) are followed the more closely the higher the temperature.

Among the factors which have to be taken into account in discussing the properties of binary systems are to be considered, besides possible chemical combination, alterations in molecular complexity, and attractions between the molecules (analogous to the a/v^2 term of van der Waals' equation) connected with alterations of "internal pressure" (compare Tammann, "Innere Kräfte und Eigenschaften der Lösungen," Leipzig, 1907). These factors may be more or less connected, but, on the other hand, the existence of unimolecular liquids indicates that there may be considerable attraction (measured by the term a/v^2) between molecules without leading to chemical combination.

The general conclusion is that at present there are no means of reaching a definite decision on this matter, and we have to depend on rather uncertain criteria which do not all point in the same direction.

282. "Preparation of Anhydrides by the Action of Thionyl Chloride on Salts of Organic Acids." (Preliminary Note). By WILLIAM SMITH DENHAM.

The author has shown (*Trans.*, 1909, xcv., 1235) that sulphur monochloride acts readily on the sodium or silver salts of organic acids in presence of indifferent solvents, forming unstable sulphur compounds of the type $(\text{R}\cdot\text{CO}_2)_2\text{S}_2$, which, on spontaneous decomposition, give anhydrides of the acids, together with sulphur dioxide and sulphur.

Since, according to one view, thionyl chloride has a constitution similar to that of sulphur monochloride, attempts have now been made to obtain compounds of the type $(\text{R}\cdot\text{CO}_2)_2\text{SO}$ by the substitution of thionyl chloride in the above reaction. Intermediate compounds of this type were not obtained, but it was found that reaction takes place smoothly and readily between typical silver salts and thionyl chloride, with evolution of sulphur dioxide and formation of the acid anhydride, probably according to the equation: $2\text{R}\cdot\text{CO}_2\text{Ag} + \text{SOCl}_2 = (\text{R}\cdot\text{CO}_2)_2\text{O} + \text{SO}_2 + \text{AgCl}$. As in this case sulphur dioxide is the only product in addition to the anhydride, this modification of the reaction possesses obvious advantages as a method of preparing anhydrides over that in which sulphur chloride is used. The reaction is carried out as described in the case of sulphur chloride, that is, by adding thionyl chloride dissolved in dry ether to a slight excess of the silver salt suspended in the same solvent, the containing vessel being cooled if necessary. After filtration from silver chloride and distillation of the ether, the anhydride is left in good yield, and generally nearly pure. In this way, acetic, benzoic, and succinic anhydrides have already been obtained.

Whilst sulphur chloride does not, under these conditions, react with silver oxalate or with silver malonate, thionyl chloride does react, but only decomposition products have been obtained.

The author proposes to apply this method to the preparation of anhydrides of hydroxy-acids and of optically active acids, and to the preparation of mixed anhydrides. Preliminary experiments indicate that this may be successfully done, and the author made this preliminary announcement in view of the fact that H. Meyer (*Chem. Zeit.*, 1909, xxxiii., 1036) outlines a method of preparing anhydrides of sulphonic acids from the corresponding alkali salts by the action of thionyl chloride.

283. "A New Synthesis of Oxazole Derivatives." By ROBERT ROBINSON.

The author has found that certain acyl derivatives of

ω -aminoacetophenone are condensed, under the influence of sulphuric acid, to oxazoles.

ω -Benzoylaminoacetophenone, prepared by benzoylating ω -aminoacetophenone, crystallises in needles, melting at 123°, and when warmed with sulphuric acid furnishes 2:5-diphenyloxazole (E. Fischer, *Ber.*, 1896, xxix., 207). ω -Phenylacetylaminoacetophenone is obtained by the action of phenylacetyl chloride on ω -aminoacetophenone stannichloride in the presence of potassium hydroxide; it forms colourless needles or prisms melting at 104°. The oxime melts at 154°, and the phenylhydrazone at 184–185°.

When ω -phenylacetylaminoacetophenone is dissolved in sulphuric acid, it gives rise to 5-phenyl-2-benzoyloxazole, crystallising in long flat needles melting at 89°; the picrate melts at 103°. α -Hydroxy- β -phenylacetylamino- α -phenylethane, $\text{OH}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\text{Ph}$, prepared by reducing ω -phenylacetylaminoacetophenone with sodium and dilute methyl alcohol, forms colourless prisms melting at 99°; it does not condense to an oxazole. On warming ω -benzoylaminoacetoveratrone with sulphuric acid, 2-phenyl-5-veratryloxazole is obtained in slender needles melting at 97°, and, in a similar manner, 2-benzyl-5-veratryloxazole, colourless needles, melting at 86°, is obtained from ω -phenylacetylaminoacetoveratrone, which melts at 135°, and is prepared from ω -aminoacetoveratrone stannichloride and phenylacetyl chloride. Reduction of 2-oximino-5:6-dimethoxy-1-hydrindone and benzoylation of the hydrochloride of the resulting 2-amino-compound furnishes 2-benzoylamino-5:6-dimethoxy-1-hydrindone, which crystallises in needles melting at 224°; the compound does not condense to an oxazole under the influence of sulphuric acid.

284. "Ethyl Benzoylacetate." By EDWARD HOPE and WILLIAM HENRY PERKIN, jun.

The authors have made a careful investigation of the conditions under which ethyl benzoylacetate is converted into mono- and di-substitution derivatives, and of the behaviour of these on hydrolysis.

NOTICES OF BOOKS.

Diamonds. By Sir WILLIAM CROOKES, LL.D., D.Sc., F.R.S. London and New York: Harper Brothers. 1909.

The origin and occurrence of diamonds are discussed in this book, which gives an account of the history of a diamond from the time the matrix containing it is excavated until it is ready for setting. The marvellous structure of the Kimberley and De Beers mines with their curious pipes is described and illustrated by plans and photographs, and the treatment of the blue ground—mining, raising to the surface, weathering, crushing, and washing—is followed in detail, concluding with the final concentrating and sorting performed by the pulsators. The chemical and physical properties of diamonds are next discussed, and the various kinds of stones which are characteristic of the different mines are described. The author has much interesting information to give relating to the phosphorescence and superficial discoloration of the stones by the bombardment of radiant matter; an account is also given of his investigations relating to the action of Röntgen rays, and of the β -rays from radium, and an examination of the question of the probable origin of the diamond follows. The results of the author's recently discovered method of preparing artificial diamonds by explosions in closed vessels are explained and illustrated, and meteoric diamonds form the subject of the last chapter.

Recent Advances in Physical and Inorganic Chemistry.

By A. W. STEWART, D.Sc. With an Introduction by Sir WILLIAM RAMSAY, K.C.B., F.R.S. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1909.

In this book Dr. Stewart shows unmistakably that at any rate in one branch of scientific literature he has no rival.

It is in one sense a companion volume to the similar work on "Recent Advances in Organic Chemistry," and in a series of articles summarises the researches of the last twenty years in inorganic and physical chemistry. Each chapter deals with some subject which has been thoroughly investigated in recent times, and which seems to have an important bearing upon the advance of the science as a whole; every chapter is interesting and stimulative, and the book will be a valuable addition to the library of the worker in other branches of chemistry who does not want entirely to lose touch with progress in other directions, and of the advanced student who is desirous of taking up some research. The style in which it is written is exceedingly clear, and if anything the author has erred on the side of presupposing too little rather than too much knowledge in his readers, and sometimes one may be pardoned for feeling slightly impatient of elementary matter—Dulong and Petit's Law in atomic weight determinations, for instance—when so much had of necessity to be left unnoticed.

L. Oertling's Illustrated Catalogue of Chemical, Assay, and Bullion Balances. 1909.

The balances made by Messrs. Oertling have been thoroughly tested in many university and other laboratories, and have been found unexceptionable in quality and workmanship; in their latest catalogue are listed and illustrated some new special balances, various forms of assay and bullion balances and physical, including vacuum balance. In addition, all appliances for use with balances—lenses for reading scale divisions, &c., are included, and standard measures of capacity and length. The catalogue should be thoroughly studied by any one who is contemplating the purchase of a new balance, and it will be forwarded post free upon application to Messrs. Oertling.

CORRESPONDENCE.

STANDARDISATION OF DISINFECTANTS.

REPORT OF *The Lancet* COMMISSION.

To the Editor of the *Chemical News*.

SIR,—If any further evidence were required that it is impossible to standardise disinfectants as a whole by any one test, it has been furnished in abundance by the Report of *The Lancet* Commissioners. Notwithstanding the large amount of chemical and bacteriological work they have done, it does not mark any advancement in respect of what was previously known concerning the subject.

The Lancet Commissioners have apparently recognised the impossibility of determining the disinfectant value of perchloride of mercury, chloride of lime, and formalin by the bacteriological test which they describe, and yet they have examined "Sanitas Fluid" by it, and classified it as a coal-tar disinfectant, although that liquid contains no coal-tar, and is quite as dissimilar in character from coal-tar preparations as are the three other articles above named. In regard to their experiments and report on coal-tar disinfectants, serious objection is to be taken against the chemical part of the investigation, inasmuch as the chemical process employed to determine the percentage of active principles in these various preparations fails to give satisfactory results. By way of proof, *The Lancet* process has been employed in our laboratories in respect of a mixture known to contain 88 per cent phenoloids, but it only showed the percentage of 60 per cent, whereas in respect of a disinfectant liquid known to contain 52 per cent, Mr. Wynter Blyth's acetone process showed it to contain 54 per cent—a much more satisfactory result—while *The Lancet* process gave only 34 per cent.

As for the bacteriological test which has been made, it simply gives the relative values of the coal-tar disinfectants which were subjected to examination in respect of *B. coli* under the special circumstances observed; just as the standardised *B. typhosus* (Rideal-Walker test gives relative

values in respect of *B. typhosus* under the special conditions observed in that test. In neither case do the results indicate the real disinfectant values of the preparations nor reproduce the conditions under which disinfection has to be carried out in practice by the medical profession and the public at large. This seems to be recognised by the Commissioners themselves, for they state that "the conditions of the test are, so far, removed from those of natural disinfection."

Up to a point I personally have little cause for complaint, for according to the results which have been published by *The Lancet* Commissioners, "Sanitas-Bactox" ranks, amongst the homogeneous liquids which were tested, equally with one other preparation, as the highest in germicidal power on the one hand, and takes top place when the cost is compared on a basis of efficiency and in ratio to carbolic acid. When, however, it is examined by the Rideal-Walker test it gives a coefficient of 20 at least, whereas the said other disinfectant only reveals a coefficient of about 15. Again, "Sanitar-Okol" takes first place amongst the coal-tar disinfectants of the emulsion order, both with respect to coefficient and comparative cost.

The bacteriological test which has been employed is really only applicable to coal-tar disinfectants, and it, in common with the so-called Rideal-Walker test, cannot be employed to ascertain the comparative values of disinfectants of other chemical composition. For example, corrosive sublimate, the manganates and permanganates, hypochlorites, sulphurous acid, formaldehyde, peroxide of hydrogen, ordinary "Sanitas fluid," and many other well known disinfectants of varying chemical nature and action are not amenable to such tests, so that their disinfectant values cannot be determined by any such method. *The Lancet* Commissioners have altogether disregarded the valuable inhibitive and antiseptic properties of the disinfectants above enumerated, and no attention whatever has been paid to their behaviour as oxidising agents, or to their chemical activities in other directions. They have also paid tribute to the autocracy of microbes, but have disregarded altogether the matter of their environment. Every student who has paid the most cursory attention to the subject knows perfectly well that disease is not produced by the mere mechanical presence of micro-organisms, but by their production through chemical reactions of definite poisonous substances, and it is these poisonous substances that constitute the true infectants of disease and not the microbes themselves. Practical disinfection therefore aims at preventing the formation of such infective material on the one hand, and of destroying it, if and when produced on the other hand, and is not confined to the mere destruction of universally distributed micro-organisms which, in their proper sphere and under proper control, constitute one of the most beneficent orders of creation.

Germicidal value, therefore, is no measure of disinfectant value; removal by washing (cleanliness) is really much more efficacious, up to a point, than destruction of microbic life by the application of germicides; so that rarely is the use of strong germicides called for, at any rate, at the hands of the public, and "Sanitas fluid" is for most of such uses more than sufficiently strong, and may often indeed be diluted with several times its own quantity of water before use. As *The Lancet* has itself recently observed, "there is no factor more favourable to successful invasion of the human body by disease-producing organisms than when the air is rendered stale, warm, and musty," but no one would dream of resorting to the use of strong coal-tar germicides for the purpose of changing the chemical character of such air. Resort would be had, of course, to the employment of a preparation like "Sanitas fluid" or peroxide of hydrogen, both of which are capable of doing what is wanted by way of germicidal action in addition to their particular value of restoring oxygen to the impure air and the destruction of foul organic matter.

The only measure of utility of any disinfectant that is

offered for public use is the extent to which it may be satisfactorily employed for the purposes for which it is advocated, and *The Lancet* Commissioners have not made any serious attempt to grapple with the problem from this the only rational standpoint.—I am, &c.,

C. T. KINGZETT, F.I.C., F.C.S., ex-Vice-President, Society of Public Analysts; Author of "Nature's Hygiene" (Baillière & Co.), &c.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlix., No. 17, October 26, 1909.

Transformations of Selenium.—Maurice Coste.—At the ordinary temperature selenium can exist in three states:—(1) Precipitated or vitreous selenium; (2) red crystallised selenium; (3) black metallic selenium. These three varieties are characterised by different densities. Metallic selenium dissolves easily in several solvents, e.g. carbon disulphide, toluene, &c., and when a solution is rapidly cooled red selenium is obtained. Vitreous selenium gives red crystallised selenium in presence of quinoline and of aniline. Vitreous selenium is transformed into metallic selenium at 98°; the author has studied the transformation by means of a dilatometer, and finds that in toluene it is completed in an hour. The density after the transformation = 4.62. (Density of vitreous selenium, = 4.30).

Hexahydrophenylacetylene and Hexahydrophenylpropionic Acid.—Georges Darzens and M. Rost.—When hexahydroacetophenone is treated with phosphorus pentachloride the chlorine derivative formed, $C_6H_{11}-CCl_2-CH_3$, is not stable, but is rapidly transformed into hexahydrochlorostyrol, $C_6H_{12}-CCl=CH_2$. When this is treated with alcoholic potash it loses HCl, and hexahydrophenylacetylene is obtained. The latter is a true acetylene hydrocarbon, and readily gives metallic derivatives. Its sodium compound fixes carbon dioxide, giving hexahydrophenylpropionic acid, of which the authors have prepared the methyl and ethyl ethers.

MISCELLANEOUS.

Julius Thomsen Memorial Lecture.—This Lecture will be delivered by Prof. Sir Edward Thorpe, C.B., F.R.S., at the Ordinary Scientific Meeting of the Chemical Society on Thursday, February 17th, 1910, at 8.30 p.m.

Electrolysis of Carboxylic Acids.—F. Kaufler and C. Herzog.—The formation of ethane by the electrolysis of acetic acid may be explained by supposing that the intermediate product is either (i.) free methyl, (ii.) acetyl peroxide, or (iii.) acetic acid anhydride. In the first case if other atoms were present which could unite with the methyl group the reaction $CH_3 + X = CH_3X$ would probably occur in addition to $2CH_3 = C_2H_6$. When acetate is electrolysed in presence of iodine no methyl iodide can be condensed, as it is diluted with other gases, ethane, carbon dioxide, &c., but it can be fixed chemically by absorption in alcoholic dimethylaniline solution. Iodine does not react with acetic acid anhydride nor with acetyl peroxide. The authors have also investigated the products of the electrolysis of haloid acetic acids and aromatic acids. Monochloroacetic acid yields methylene chloride by a process analogous to that which occurs with the unsubstituted acid.—*Berichte*, xlii., No. 14.

MEETINGS FOR THE WEEK.

TUESDAY, 28th. } Christmas Lectures (adapted to a juvenile auditory).
THURSDAY, 30th. } "Modern Electricity," by W. Duddell, F.R.S.

THE CHEMICAL NEWS.

VOL C., No. 2614.

OUR HUNDREDTH VOLUME.

THE present number of the CHEMICAL NEWS completes the fiftieth year of its existence and the one hundredth volume. In our next number we shall give a short survey of the position of chemistry during the earlier years of the CHEMICAL NEWS. In the meantime it is exhilarating to receive so abundant a recognition of our life-long labours as recorded in the following communications:—

“THE CHEMISTS’ CLUB OF NEW YORK.

“November 27th, 1909.

“This is to certify that at a meeting held on November 27th, 1909, the Chemists’ Club of New York elected Sir William Crookes Honorary Member in recognition of his eminent services to the Science of Chemistry.

MORRIS LOEB, President.

PARKER C. McILHINEY, Secretary.”

“The Chemists’ Club of the City of New York extends to Sir William Crookes of London hearty congratulations upon the completion of the one hundredth volume of the CHEMICAL NEWS, which, under his direction, has been so successfully devoted for a half century to the diffusion of facts which may tend to improve and augment our knowledge of the Arts and Sciences upon which most of the operations of civilised life are based, and its Members wish for him not only many more years in such fruitful service, but that they and other men of Science may profit by further additions to his already long list of rich contributions to theoretical, specialised, and practical scientific knowledge.

MORRIS LOEB, President.

PARKER C. McILHINEY, Secretary.”

(Followed by the autograph signatures of 92 Members of the Chemists’ Club of New York).

“AMERICAN CHEMICAL SOCIETY.

“Office of the Secretary,

“Durham, N.H., December 2nd, 1909.

“Sir WILLIAM CROOKES, London, England.

“MY DEAR SIR,—By a recent unanimous vote of the Council, we take great pleasure in extending to you cordial greetings and hearty congratulations on the Jubilee Anniversary of your successful Editorship of the CHEMICAL NEWS.

“We desire also to express our personal appreciation of your labours in the cause of Chemistry, and take especial pride that you are a Member of our Society.—Sincerely yours,

WILLIS R. WHITNEY, President.

CHARLES L. PARSONS, Secretary.”

Action of Metallic Magnesium on Acetylene.—J. Novák.—When magnesium acts on acetylene the product varies according to the experimental conditions; magnesium carbide which gives acetylene with water may be formed, or a substance which gives allylene with water, and which may be magnesium allylide or a hitherto unknown carbide. The action of different alcohols, hydrocarbons, &c., also gives products which are decomposed by water, yielding acetylene or allylene, and which are being further studied.—*Berichte*, xlii. No. 15.

A METHOD FOR THE IODOMETRIC DETERMINATION OF SILVER BASED UPON THE REDUCING ACTION OF POTASSIUM ARSENITE.

By ROWLAND S. BOSWORTH.

IT is well known that an ammoniacal solution of silver arsenite deposits metallic silver when the ammonia is evaporated by boiling. During this reaction, by which the silver salt is reduced, the arsenious acid becomes oxidised to the higher condition of oxidation, where arsenic has a valence of five, according to the equation $2Ag_2O + As_2O_3 = As_2O_5 + 4Ag$. The present paper deals with some work done with the purpose of determining whether this reaction was quantitative, and of devising a rapid iodometric method for the determination of silver based upon the reduction of the silver salt to the metal.

Experiments were first performed upon a silver nitrate solution of known strength according to the following plan:—To a definite portion of a standard solution of silver nitrate was added a known volume of a standard potassium arsenite solution in excess of the amount necessary to reduce the silver salt present. Ammonia was then added in sufficient quantity to dissolve the precipitate formed, and the resulting solution was diluted to 100 cc., and boiled until the escaping vapour gave no test for free ammonia with moistened litmus-paper. The solution, out of which metallic silver had then separated, was filtered, cooled, and made faintly acid in order to neutralise any possible trace of ammonia which might remain. After making alkaline with sodium bicarbonate, the excess of potassium arsenite was titrated with N/10 iodine. The silver value of the iodine used was subtracted from that of the potassium arsenite originally taken, and the result used as a measure of the silver present. In Table I., A, are given the results of experiments performed in the manner described above.

The effect was next tried of the use of sodium bicarbonate as a means for producing alkalinity in place of the ammonia. The following procedure was used:—To a solution of silver nitrate was added an excess of standard potassium arsenite solution. The mixture was made alkaline by means of 25 cc. of a saturated solution of sodium bicarbonate, diluted to 100 cc., and boiled until the precipitate of silver arsenite was converted to metallic silver. The solution was then filtered and acidified, in order to break up the neutral carbonate formed by boiling the bicarbonate. Finally, the solution was made alkaline with sodium bicarbonate, and the potassium arsenite present was titrated with N/10 iodine, the titration giving a measure of the silver originally taken. The details of these experiments are given in Table I., B.

Since the precipitate of metallic silver, in the experiments of both A and B, was in a well coagulated condition, experiments were carried on in which filtration was omitted, the titration being made in the presence of the precipitate. The results given in Table II., A and B, show that the precipitate has no appreciable effect upon the titration. If nitric acid were present in the solution of the silver salt, as is usually the case in analysis, it would be converted to a nitrate by the addition of the alkali. In order to prove that the presence of a considerable amount of sodium nitrate would not hinder the reduction of the silver salt, determinations were made after the addition of 2 grms. of that substance, with the uniformly good results shown in Table II., C.

Since in analysis it is often necessary to determine silver when copper or lead or both are also present in solution, and since silver can, with proper precautions, be separated from either of these metals by precipitation with hydrochloric acid, it seemed desirable to accomplish the reduction of silver when it was in the form of the chloride. Consequently, determinations were made according to the following plan, the details of the experiments being given

TABLE I.

Silver taken. Grm.	KH ₂ AsO ₃ added.		I ₂ used.		Silver found. Grm.	Error in terms of silver. Grm.
	Cc.	Silver value. Grm.	Cc.	Silver value. Grm.		
A.—Use of NH ₄ OH with Filtering.						
0.1054	20	0.2000	8.53	0.0949	0.1051	− 0.0003
0.1054	20	0.2000	8.52	0.0948	0.1052	− 0.0002
0.1054	30	0.3000	17.42	0.1939	0.1061	+ 0.0007
0.1159	20	0.2000	7.60	0.0846	0.1154	− 0.0005
0.1054	21	0.2100	9.37	0.1043	0.1057	+ 0.0003
0.1054	20	0.2000	8.48	0.0944	0.1056	+ 0.0002
B.—Use of NaHCO ₃ with Filtering.						
0.1054	15	0.1618	5.65	0.0571	0.1047	− 0.0007
0.1054	23	0.2481	14.14	0.1430	0.1051	− 0.0003
0.1054	12	0.1295	2.40	0.0243	0.1052	− 0.0002
0.1054	15	0.1618	5.60	0.0566	0.1052	− 0.0002
0.1054	15	0.1618	5.55	0.0561	0.1057	+ 0.0003
0.1054	20	0.2158	10.91	0.1104	0.1054	± 0.0000
0.2635	35	0.3776	11.33	0.1146	0.2630	− 0.0005

TABLE II.

A.—Use of NH ₄ OH. Titration carried on in presence of the Precipitate.						
0.1054	20	0.2000	8.55	0.0952	0.1048	-0.0006
0.1054	20	0.2000	8.50	0.0946	0.1054	±0.0000
0.1054	23	0.2300	11.28	0.1256	0.1044	-0.0010
0.1054	20	0.2000	8.45	0.0941	0.1059	+0.0005
0.1054	20	0.2000	8.48	0.0944	0.1056	+0.0002
B.—Use of NaHCO ₃ . Titration carried on in presence of the Precipitate.						
0.1054	18	0.1800	6.80	0.0757	0.1043	-0.0011
0.1054	17	0.1709	5.81	0.0647	0.1053	-0.0001
0.1054	15	0.1500	4.00	0.0445	0.1055	+0.0001
0.1054	21	0.2100	9.45	0.1052	0.1048	-0.0006
0.1054	25	0.2500	13.00	0.1447	0.1053	-0.0001
0.1054	31	0.3100	18.40	0.2048	0.1052	-0.0002
C.—Use of NaHCO ₃ . 2 grms. of NaNO ₃ present. Titration carried on in presence of Precipitate.						
0.0949	21	0.2100	10.42	0.1160	0.0940	-0.0009
0.1054	21	0.2100	9.43	0.1050	0.1050	-0.0004
0.1265	20	0.2000	6.60	0.0735	0.1265	±0.0000
0.1686	21	0.2100	3.80	0.0432	0.1678	-0.0008
0.1054	15	0.1500	4.08	0.0454	0.1046	-0.0008

TABLE III.

A.—Reduction of Precipitated AgCl.						
0.1017	15	0.1619	5.40	0.0599	0.1020	+0.0003
0.1017	15	0.1619	5.44	0.0603	0.1016	-0.0001
0.1017	15	0.1619	5.40	0.0599	0.1020	+0.0003
0.1017	15	0.1619	5.42	0.0601	0.1018	+0.0001
0.1017	17	0.1834	7.44	0.0825	0.1009	-0.0008
B.—Reduction of AgCl Precipitated in the presence of 0.09 gm. of Copper.						
0.1017	15	0.1619	5.41	0.0600	0.1019	+0.0002
0.1017	15	0.1616	5.44	0.0603	0.1016	-0.0001
0.1017	15	0.1619	5.39	0.0598	0.1021	+0.0004
C.—Reduction of AgCl Precipitated in the presence of 0.2 gm. of Lead.						
0.1220	16	0.1726	4.57	0.0507	0.1219	-0.0001
0.1108	15	0.1619	4.60	0.0510	0.1109	+0.0001
D.—Reduction of AgCl Precipitated from a Solution containing 0.09 gm. of Copper and 0.2 gm. of Lead.						
0.1017	15	0.1619	5.45	0.0604	0.1015	-0.0002

in Table III., A. :—From a known amount of a standard solution the silver was precipitated with hydrochloric acid and filtered upon asbestos. The precipitate was then acted upon by strong ammonia, the mixture being allowed to stand until the silver chloride was completely dissolved. The solution was diluted to 100 cc., and reduction accomplished by adding an excess of standard potassium arsenite and boiling the resulting solution. The excess of potassium arsenite was subsequently titrated according to the procedure outlined previously in this paper. In Table III., B, are details of determinations similarly made, in which the silver was separated from 0.09 gm. of copper. The experiments in Table III., C, illustrate the separation of silver from 0.2 gm. of lead, and in the experiment recorded in D the silver was precipitated from a solution containing 0.09 gm. of copper and 0.2 gm. of lead.

From the results recorded in this paper, it is evident that silver can be easily and accurately estimated, either in solution or in the form of the precipitated chloride, by adding an excess of standard potassium arsenite, boiling in alkaline solution to accomplish the reduction of the silver salt to metallic silver, and titrating the excess of potassium arsenite with iodine. The silver value of the iodine used is to be subtracted from that of the potassium arsenite originally taken, the result giving the amount of silver present.—*American Journal of Science*, xxvii., p. 287.

A METHOD FOR THE IODOMETRIC ESTIMATION OF SILVER BASED UPON THE USE OF POTASSIUM CHROMATE AS A PRECIPITANT.

By F. A. GOOCH and ROWLAND S. BOSWORTH.

It has been shown in a previous paper that with proper precautions silver may be precipitated and accurately estimated as silver chromate. It was found that the addition of a sufficient excess of potassium chromate to a solution of silver nitrate, even in the presence of small amounts of nitric acid, brings about a complete precipitation of the silver as silver chromate, and that the precipitate thus obtained may be transferred to the asbestos filter by means of a dilute solution of potassium chromate, and washed with small amounts of water without appreciable loss of silver chromate. Upon the basis of such exact precipitation of silver chromate by potassium chromate it should be possible to establish a method for the iodometric estimation of silver, either by the estimation of the chromic acid ion of the precipitated and washed silver chromate, or by the determination of the chromic acid ion of the potassium chromate which remains after the precipitation of the silver salt by a known amount of standard potassium chromate.

TABLE I.

Silver taken.		K ₂ CrO ₄ used.	Na ₂ S ₂ O ₃ used.	Silver found.	Error in terms of silver.
Volume of solution.	Weight.				
Cc.	Grm.	Grm.	Cc.	Grm.	Grm.
20	0.1261	0.3039	26.54	0.1262	+0.0001
25	0.1576	0.3039	22.61	0.1575	-0.0001
15	0.0946	0.3293	30.51	0.0946	—
15	0.0946	0.3293	30.60	0.0940	-0.0006
15	0.0946	0.3293	30.57	0.0941	-0.0005
15	0.0946	0.3293	30.55	0.0945	-0.0003
19.98	0.1260	0.3293	32.20	0.1255	-0.0005
20	0.1201	0.3293	32.09	0.1263	+0.0002
20	0.1261	0.3293	32.10	0.1263	+0.0002
25	0.1576	0.3293	27.30	0.1576	—

In studying the latter procedure a known amount of standard potassium chromate in excess of the amount needed to precipitate the silver was added to the solution of silver nitrate. The precipitate was dissolved in

TABLE II.

Silver taken.		K_2CrO_4 .		$NaNO_3$ present.	$Na_2S_2O_3$ used.	Silver found.	Error in terms of silver.
Volume of solution.	Weight.	Volume	Weight.				
Cc.	Grm.	Cc.	Grm.	Grms.	Cc.	Grm.	Grm.
10	0.1101 (a)	37	0.2436 (a)	1	20.47 (a)	0.1107	-0.0006
10	0.1101	37	0.2436	1	20.53	0.1103	+0.0002
10	0.1101	25	0.1647	1	9.07	0.1097	-0.0004
10	0.1101	27	0.1778	1	11.02	0.1096	-0.0005
15	0.0862 (b)	+30	0.1974 (a)	2	17.14 (a)	0.0859	-0.0003
15	0.0862	30	0.1974	1	17.05	0.0865	+0.0003
15	0.0862	30	0.1974	1	17.14	0.0859	-0.0003
25	0.1437	50	0.3294	10	28.53	0.1435	-0.0002

(a) Approximately N/10.

(b) Approximately N/20.

TABLE III.

Silver taken.		HNO_3 present.	K_2CrO_4 weight.	$Na_2S_2O_3$ used.	Silver found.	Error in terms of silver.
Volume of solution.	Weight.					
Cc.	Grm.	Grm.	Grm.	Cc.	Grm.	Grm.
25	0.1348	0.063	0.60	18.35	0.1342	-0.0006
20	0.1078	0.063	0.65	14.67	0.1073	-0.0005
15	0.0808	0.063	0.65	11.06	0.0809	+0.0001
15	0.0808	0.063	0.65	10.96	0.0802	-0.0006
20	0.1078	0.063	0.65	14.67	0.1073	-0.0005
30	0.1618	0.063	0.75	22.02	0.1610	-0.0008
20	0.1078	0.063	0.65	14.71	0.1075	-0.0003
25	0.1348	0.063	0.65	18.41	0.1347	-0.0001
25	0.1348	0.063	0.65	18.41	0.1347	-0.0001
20	0.1078	0.063	6.65	14.74	0.1078	—

ammonia, and re-precipitation brought about by boiling to a volume of 10 to 15 cc. The second, crystalline precipitate was filtered upon asbestos, and washed with the least possible amount of water applied in small portions successively. The filtrate was treated with potassium iodide and acidified with sulphuric acid. The iodine set free was titrated with sodium thiosulphate. The difference between the silver value of the iodine thus found and that of the potassium dichromate used was taken as the measure of the silver present. In Table I. are given the details of experiments performed in accordance with this procedure.

In Table II. are given the details of similar experiments in which the precipitation was effected in the presence of sodium nitrate.

Since, as has been shown in the paper previously referred to, relatively large amounts of potassium chromate are necessary to bring about complete precipitation of the silver chromate in the presence of nitric acid, the above procedure seemed less adapted to the determination of silver in a solution containing that acid than the method whereby the precipitated and washed silver chromate is determined. The following is an account of the results obtained in the study of this latter procedure. To the silver solution containing free nitric acid, potassium chromate was added in excess of the amount necessary to take up the nitric acid with formation of potassium dichromate. The precipitate was dissolved in ammonia, and re-precipitation effected by boiling to a volume of 10 to 15 cc. The second, crystalline precipitate was transferred to an asbestos filter by means of a dilute solution of potassium chromate, washed with the least possible amount of water applied in small portions successively, and dissolved in a few cc. of a strong solution of potassium iodide. The solution in potassium iodide was diluted and acidified with sulphuric acid. The iodine set free was titrated with sodium thiosulphate, and taken as the measure of the silver present. In Table III. are given the details of experiments made in this manner.

The results obtained justify the conclusion that silver can be accurately estimated by precipitating as silver chromate with the use of a sufficient excess of potassium chromate, dissolving the precipitate formed in ammonia, re-precipitating by boiling to low volume, and determining

iodometrically either the chromate ion in combination with the silver or the chromate ion of the potassium chromate remaining after precipitation of the silver with a known amount of standard potassium chromate.—*American Journal of Science*, xxvii., 302.

ELECTRO-DEPOSITION OF SOME METALS FROM ACETONE SOLUTION.*

By HARRISON E. PATTEN and WILLIAM ROY MOTT.

CONTINUING our previous work on the electrolysis of metallic salts dissolved in non-aqueous solvents (see Note 1), the following experiments were carried out. Saturated solutions in acetone were made, using as solutes NaI, SrI_2 , $CdCl_2$, $FeCl_3$, $CuCl_2$, $SnCl_2$, $SbCl_3$, and $BiCl_3$. These were electrolysed between platinum electrodes to ascertain whether the metal would deposit or not; and if so, at what current density and cathode polarisation. Similarly, a solution of $AsCl_3$ in acetone, about 10 per cent by volume, was electrolysed, and a good deposit of arsenic secured, but the cathode and anode discharge potentials were not obtained owing to interruption of the work.

The general methods used for determining the decomposition voltage, anode and cathode polarisation, and discharge potentials, have been given in our former papers (see Note 2). Table I. contains a summary of the results of the present investigation.

Smooth deposits of cadmium, tin, antimony, bismuth, and arsenic were obtained at low current densities, the tin showing a marked tendency to tree at higher current densities. The deposits have not been tested for adherence, behaviour under buffing, or for carbon content, as this paper is essentially a preliminary survey. The deposition of sodium (Note 3) and of strontium is interesting, as we

* A Paper presented at the Fifteenth General Meeting of the American Electrochemical Society, at Niagara Falls, Canada, May 6-8, 1909.

TABLE I.—Summary of Data on Electrolysis of Metallic Chlorides and Iodides in Acetone between Platinum Electrodes.

Current density. Amperes per sq. cm.	Polarisation of cell.			Temp. (°C.).	Solute.	Remarks.
	Anode volts.	Cathode volts.	Total volts.			
0.100	-0.70	+1.10	+1.7	28	NaI	
0.100	-1.10	+1.10	+2.20	—	NaI	
0.200	-0.90	+2.20 D	+3.1	26	NaI	Na deposited.
0.1	-0.70	+0.50 D	+1.1	28	SrI ₂	
0.2	-0.70	+2.20 D	+2.90	28	SrI ₂	Sr deposited.
0.001	-1.79	-0.12	+1.5	—	CdCl ₂	Cd deposited.
0.000	-0.751	-0.751	+0.00	27	FeCl ₃	
0.010	-0.85	-0.75	+0.3?	—	FeCl ₃	
0.060	-1.10	-0.40	+0.40	—	FeCl ₃	
0.200	-1.17 D	-0.06 D	+1.20?	—	FeCl ₃	Fe deposited.
			+1.50			
0.000	-0.90	-0.90	0.00	—	CuCl ₂	
0.100	-1.06 D	-0.04 D	+1.02	—	CuCl ₂	Cu deposited.
0.001	-1.00	-0.18	+0.8	—	SnCl ₂	Sn deposited.
0.010	-3.10	-0.18	+2.9	26	SnCl ₂	
0.100	-3.60	-0.18	+3.3	—	SnCl ₂	Sn trees.
0.010	—	—	+2.8	—	SnCl ₂	
0.100	—	—	+3.6	—	SnCl ₂	Sn trees.
0.0007	-1.98	-0.22 D	—	22	SbCl ₃	Sb deposited.
0.0013	-2.05	-0.22 D	—	—	SbCl ₃	
0.0023	-2.01	-0.27	—	—	SbCl ₃	
0.028	-1.71 D	-0.18 D	—	22	BiCl ₃	Bi deposited.
0.0136	—	—	+2.01	28	AsCl ₃	As deposited; no trace of AsH ₃ by AgNO ₃ test.

D = Discharge potential, current passing.

TABLE II.—Decomposition Curves of Anhydrous Arsenic Trichloride* in Acetone.

Temperature, 28° C.

Distance apart of electrodes = 3 cm.

Area of each Pt electrode = 3 sq. cm.

Curve I.		Current density.	Curve II.		Current density.
Volts.	Amperes.†	Amperes.	Volts.	Amperes.‡	Amperes.
0.30	0.000012	0.000004	0.5	0.0003	0.0001
0.55	0.000087	0.000029	1.00	0.0008	0.00026
0.82	0.000197	0.000066	1.50	0.0017	0.00056
1.20	0.000395	0.000132	2.00	0.003	0.001
1.27	0.000546	0.000182	2.50	0.0042	0.0014
1.42	0.000622	0.000207	3.00	0.006	0.002
1.46	0.000740	0.000246	3.50	0.007	0.0023
1.51	0.000872	0.000290	4.00	0.0088	0.0029
1.63	0.00103	0.00031	4.50	0.0103	0.0034
1.74	0.00126	0.00042	5.00	0.012	0.004
1.79	0.00166	0.00055	5.50	0.0135	0.0045
2.01	0.00207	0.00069	6.00	0.015	0.005
2.07	0.00246	0.00082	6.50	0.016	0.00503
2.10	0.00289	0.00096	7.00	0.018	0.0060
2.61	0.00392	0.00131	7.50	0.0197	0.0069
3.36	0.00642§	0.00214	8.00	0.021§	0.007
			8.50	0.0225	0.0075
			9.00	0.0241	0.0080
			9.50	0.0257	0.0086
			10.00	0.027	0.009
			10.5	0.0285	0.0093
			11.0	0.030	0.010
			11.5	0.0314	0.0105
			12.0	0.033	0.011
			13.0	0.0356	0.0118
			14.0	0.0382§	0.0127§
			15.0	0.041	0.0136

* AsCl₃ dissolves with evolution of considerable heat. The concentration was about 10 per cent by volume.

† Determined by potentiometer.

‡ Determined by milliammeter.

§ No gas evolved.

|| Battery point 2.01 volts for total cell at this current density.

were able to secure a cathode polarisation value for each metal during its deposition, which is near the value to be expected from theoretical considerations. The current density required to deposit each of these metals is 20 amperes N.D., or about 180 amperes per square foot. Iron required 20 amperes N.D., and copper 10 amperes N.D. for deposition, but when finally they came out at these high current densities the coatings were smooth. Copper deposited from aqueous solution would be crystallised at current densities much lower than that used here—90 amperes per square foot.

Table II. gives the current electromotive force curves obtained on electrolysis solution of arsenic trichloride in acetone. The total polarisation shown by discharge was 2.01 volts, indicating that the arsenic deposit has a low single potential, as would be expected.

This work may be summarised:—

1. Sodium and strontium metals have been deposited from saturated solution of the iodides in acetone at room temperature, using rather high current density.
2. Cadmium, tin, antimony, bismuth, and arsenic have been deposited from solutions of their chlorides in acetone at moderately low current density.
3. Iron and copper were deposited from solutions of their chlorides (-ic) in acetone at rather high current densities.
4. In most cases anode and cathode polarisation values were obtained.
5. A new compound, NaI.3(CH₃)₂CO, is described.

This work was carried out in the University of Wisconsin, in the laboratories of Applied Electrochemistry and of Physical Chemistry jointly, and the authors wish to express their appreciation of the courtesy thus extended to them.

Notes.

1. "Single Potentials of Zinc in Aqueous Solutions" (*Trans. Am. Electrochem. Soc.*, 1903, iii., 317); "Experimental Determinations of the Single Potentials of the

Alkali Metals — Sodium and Potassium" (*Electro-chemical Industry*, September, 1903); "Decomposition Curves of Lithium Chloride and the Electro-deposition of Lithium" (*Journ. Phys. Chem.*, 1904, viii., 153); "On the Deposition of Zinc from Zinc Chloride Dissolved in Acetone" (*Ibid.*, 1904, viii., 483); "An Analytical Study on the Deposition of Aluminium from Ethyl Bromide Solution" (*Ibid.*, 1904, viii., 548); "The Deposition of Metallic Calcium from Alcoholic Solutions" (*Electrochem. Industry*, 1903, i., 418); "The Deposition of Sodium from a Solution of Sodium Iodide in Acetone" (*Ibid.*, 1903, i., 419); "The Electrolytic Reduction of Nitric Acid" (*Trans. Am. Electrochem. Soc.*, 1907, xii., 325); "Decomposition Curves of Lithium Chloride in Acetone—the Effect of Water" (*Journ. Phys. Chem.*, 1908, xii., 49); "Single Potentials of the Halogen Elements" (*Trans. Am. Electrochem. Soc.*, 1904, v., 73); "On the Heat of Solution of Aluminium Bromide in Ethyl Bromide" (*Trans. Am. Electrochem. Soc.*, 1905, vii., 177).

2. "Potentials of Zinc in Aqueous Solutions"; "Decomposition Voltage of Lithium in Alcohols and the Electro-deposition of Lithium"; "Electro-deposition of Lithium from Pyridine and from Acetone—the Role of Water."

3. Sodium iodide was found to form with acetone a compound which exists in equilibrium with the acetone solution saturated with respect to itself below 14° C.; the compound crystallises in long needles and has a composition corresponding to the formula $\text{NaI} \cdot 3(\text{CH}_3)_2\text{CO}$. It loses acetone in the air and reverts to NaI anhydrous. The transition value 14° C. was determined by measuring the vapour pressure of the system, $\text{NaI}-(\text{CH}_3)_2\text{CO}$, at various temperatures; on plotting a t - p curve, a nick was found at about 14° C., and it was observed that the long needles of $\text{NaI} \cdot 3(\text{CH}_3)_2\text{CO}$ had changed to the cubical anhydrous NaI just above 14° C. These measurements and the analytical data for the composition of the $\text{NaI} \cdot 3(\text{CH}_3)_2\text{CO}$ were lost in moving and have not yet been repeated (H. E. Patten).

THE PURIFICATION OF WATER SUPPLIES BY THE USE OF HYPOCHLORITES.

By WILLIAM PITT MASON, M.D.

THERE is no question but those of us who have taken ground as opposed to the "disinfection" of water by "bleach," hypochlorite of sodium, or other similar substances, must change our position. The experimental work in France and England, the improvement of the water of Bubbly-Brook at the Chicago Stock Yards, and, above all, the remarkable results secured by the Jersey City Water Supply Co., when operating upon the entire municipal supply of Jersey City, suffice to silence opposition to what may be termed the most recent purification method of to-day.

It is true that some years ago the "Woolf" process was proposed, whereby an electrolysed salt solution was employed for addition to either sewage or water; and still further back the "Webster" plan was advocated; but none of the hypochlorites was exploited in the systematic and exhaustive manner that has been recently accomplished, nor has the smallness of the "dose" that will accomplish efficient treatment ever been suspected. Let the following facts speak for themselves:—

Lake water was treated with increasing "doses" of "bleaching-powder" equivalent to the amount of available chlorine indicated. It was then allowed to stand three hours in the dark, shaken, and sowed for "total count" of bacteria.

Numerous similar sowings were made and even lower counts of residual germs were found.

Upon examining waters charged with pure cultures of *Bacillus coli communis*, and others contaminated with fresh fecal material of human origin, no gas-forming

Dose of bleach.		Bacteria per cc.
Grains per gallon.	Parts per million.	
0	0	102,900
3/100	0.51	410
1/20	0.85	320
1/10	1.70	175
1/8	2.12	100
1/4	4.25	95
1/2	8.50	45

bacteria of any kind were found alive in any instance after the use of even the smallest dose of "bleach" shown above.

Other experimenters have reached similar conclusions with still smaller doses of "available chlorine." The most satisfactory test of the process, however, is the practical one of treating the entire municipal supply daily furnished to Jersey City. The dose there used during the month of December, 1908, averaged approximately 0.03 grain available chlorine per gallon and has since been materially reduced. While using the above amount the daily counts of bacteria for the month were:—

Raw Water.	
Maximum	1600
Minimum	240
Average..	559
Treated Water.	
Maximum	30
Minimum	0
Average..	2.7

No part of this minute dose of hypochlorite reaches the consumer, and protection against pathogenic organisms appear to be assured.

It is not expected that the process will take the place of filtration because it does not aid in improving the physical appearance of a water, but as an adjunct to a filter plant there can be no question of its usefulness in times of emergency, and it can surely be depended upon to render a reasonably polluted water safe for domestic purposes, and do it at a moderate price.

It goes without saying that the hypochlorite of sodium, obtained by electrolysis of a solution of common salt, can be substituted for the bleaching-powder whenever local conditions allow of its cheap manufacture. The effect upon bacterial life is the same.—*Proceedings of the American Philosophical Society*, xlviii., No. 191.

ANTI-PUTRESCENT EFFECTS OF COPPER.

By ALFRED SPRINGER, Ph.D.,
Assisted by ALFRED SPRINGER, Jun.

FOLLOWING a discussion before the Cincinnati Section of the American Chemical Society as to whether the peculiar behaviour of a certain Cincinnati certified milk, most largely used in that city, warranted the suspicion that it contained an antiseptic, I started a series of experiments both with certified milk and check ones with milk from one of my cows, which I watched carefully so it could not be tampered with. Under like conditions these milks behaved with marked difference. After making several incineration analyses of the certified milk, I found a trace of copper therein, but its presence was not sufficiently conclusive, because the copper chlorides are more or less volatile. I therefore digested a half litre of certified milk with 350 cc. of sulphuric acid in a Kjeldahl flask, heating the same without addition of any extraneous oxidisers twelve days until it had become practically colourless, then drove off almost all of the sulphuric acid. Placing the residue in a beaker, after diluting it with water, I electrolysed it. The

deposit on the cathode was then dissolved in hydrochloric acid, the excess of hydrochloric acid driven off, and then dissolved in water. To this was added potassium ferrocyanide, and the iron and copper ferrocyanide separated by means of ammonia. I then filtered out the dissolved cupric ferrocyanide, allowed the excess ammonia to evaporate, and obtained a decided copper reaction with every bottle of certified milk I examined, although the amounts varied considerably. From a half litre of milk the copper and traces of iron, which always deposited on the cathode, hardly ever weighed more than 2 mgrms., but generally much less, therefore its exact weight could not be estimated. I then made check experiments with milk from my cow, but could find no copper, although the methods of analysis were exactly similar. In order to convince myself that only to the presence of this substance could be attributed the strange behaviour of certified milk, I started a series of experiments, first with copper salts, afterwards with copper spirals placed in the milk. While copper salts have been used for antiseptic purposes, their particular application to milk have not received proper attention. Provided these salts or metallic copper come in contact with milk, immediately after milking, most deep-seated reactions take place; however, if the milk is allowed to stand a very short time and become infected with numerous lactic bacteria, the cupric salts cannot suppress these unless abnormally large amounts thereof are used.

I observed when ammonium hydrate, in quantities of 0.1 to 0.15 per cent, is added to milk treated with copper salts, a reddish brown change of colour gradually takes place therein and the underlying liquid becomes turbid. Where no copper is in the milk this change does not take place. This reaction is most pronounced, and affords a good test for the detection of copper in milk. Should, however, ammonium hydrate to the extent of more than 0.2 per cent be added, milks with and without copper gradually assume the reddish brown colour, but only those containing copper become turbid. The most marked change produced by the presence of copper is that the milk retains its sweet odour even after the acidity contents are sufficiently high to curdle it. The milk then becomes covered with moulds, and the odour becomes decidedly nutty without trace of putrescence.

Having now satisfied myself that the certified milk contained copper, and having employed methods which indubitably proved its presence, I next determined to find out where and how it was added to the milk in a manner to escape detection by the Milk Commission; furthermore, whether it was added with the intention to deceive, or whether the dairymen were themselves the innocent victims of a process they employed. My son, Alfred Springer, jun., assisted me in most of the coming experiments, and I herewith wish to acknowledge the services rendered by him.

Supplying ourselves with some absolutely clean broad-mouthed glass-stoppered bottles, we went to Lebanon, August 10th, to inspect the dairy in question. We found it a model of cleanliness in every respect. Having the presence of copper uppermost in our minds, we examined the various possibilities of its addition. The Star cooler, made of tinned copper, was the first apparatus that suggested itself as capable of supplying some. An examination thereof showed that the tin had partly worn off at some few places, and that the filling valves were made of brass. We then followed the steam-pipes used for the cleaning of the bottles, the sterilisation of the pails, the straining cloths, and the cloths for wiping the udders of the animals. The pipes were iron, but all of the gate valves brass.

The superintendent accompanied us through the dairy, and willingly complied with all of our requests. We asked that several cows be milked direct into the bottles we had brought along, so that the milk would not come in contact with any utensil they had in the building. This was done and called raw milk. Then we asked for two bottles of

milk which, in the usual mode of procedure, had only gone through their straining cloth into the pails. This we called strained milk. We then took two bottles of milk which had passed through the Star cooler. All these bottles were immediately placed in their ice room, then packed in ice and taken to my laboratory; we there sub-divided them by running 25 cc. in two-ounce bottles, leaving some closed in the ice-chest and others at room temperature. I also made Kjeldahl digestions of the three kinds. The strained and the certified showed the presence of copper but not so the raw, thus proving that the copper had already entered through the straining cloths and the pails. The raw milk both in the ice-chest and at room temperature, as indicated by titrations with decinormal solutions of sodium hydrate, was much better than the strained or the certified. Both the strained and certified turned the second day at room temperature, the whey separating completely, whereas the raw milk remained sweet three days, and then turned normally. In the ice-chest the raw showed great superiority over the strained and certified. These experiments indicated a most undesirable state of affairs, the danger of which cannot be over-estimated, namely, that even in a dairy, like that at Lebanon, where all precautions for absolute cleanliness are scrupulously followed, a milk taken directly from the cow, bottled, and iced, should be so much superior to others set out from ten to fifteen minutes in the dairy atmosphere. It showed that the atmosphere of the dairy was charged with bacteria and spores of moulds which quickly found their way into the milk. We then determined to make a still more crucial test, and visited the dairy August 18th, first having supplied ourselves with perfectly clean bottles, which we brought with us. We asked the superintendent to milk six cows, part milked direct into the bottles, part through the straining cloths into the pails, and the rest sent through the Star cooler before any other passed over it. Some of the bottles which had been directly filled were immediately closed and others left open in the dairy fifteen minutes. Furthermore, we took samples of the condensed steam at the washing and sterilising rooms, also of such used to sterilise the cooler. The various milks, all from the same cows, were taken to my laboratory and sub-divided into 152 two-ounce bottles with 25 cc. in each, some set out open, others closed in the ice-chest, and at room temperature, some treated with ammonia, and others left for the growth of moulds. The results on the charts indicate that an exceptionally good milk direct from the udders of the cow had greatly deteriorated during the short exposure before bottling in the usual mode of procedure.

We examined the samples of water, and found that the first one, condensed at the washing-room, used to sterilise the bottles, pails, and cloths, contained part of the boiler compound mechanically carried over, and copper. The condensed water used to sterilise the cooler also showed the presence of copper. We next examined the boiler compound used at this dairy, and, strange to say, found that it contained copper salts, and was really largely at the bottom of the whole trouble. The priming or passage of foam carried this copper over to the washing and sterilising room, thus contaminating the cloths, bottles, and pails used.

While no exhaustive experiments have been made to determine whether copper is unsanitary in such small amounts as I found in the certified milk, the very fact that it changes the normal characteristics of the milk should be sufficient for its exclusion. In certified and inspected milk dairies the so-called sterilisation processes are produced by means of live steam. In many of these dairies the feed water is hard, and the use of boiler compounds becomes necessary; these frequently prime over even through pipes connected with the steam-drum. Every ingredient of a boiler compound, whatever it is, ought to be rigidly excluded from contaminating the sterilised cloths, pails, or other apparatus. This can effectually be done by interposing a still, fed directly with water, and heating it with closed steam from the boiler. This still and all pipes

leading to the sterilising apparatus should be made of block-tin.

While examining the certified milk I made quite a number of experiments with copper salts. The one great fact which always loomed up was that they, even in quantities of one part in two millions, act as antiseptics to putrescent bacteria. Organic matter in solution seldom oxidises directly to its final stage, but passes through intermediate conditions whereby the more complex forms are broken down. Putrefaction is practically limited to the fermentation of albumenoid substances, and is largely a hydrolytic change caused by the energy of anaerobic organisms, while decay results from aerobic microbial activity.

In order to test the efficiency of copper salts I made the following experiments, keeping check ones without the copper:—Egg albumin and water, blood albumin and water, egg albumin, pancreatine and water, blood albumin, pancreatin and water, chopped meat in water, eggs placed in cupric sulphate solution, egg and blood albumin with sewage, milk with sewage. In every case the copper salts displayed either greatly retardative or marked inhibitive properties towards the putrefactive bacteria, although in some cases the strength of the solution was insufficient to prevent putrefaction gradually setting in. It seems to me that this property possessed by cupric salts is of great therapeutic value, and ought to be carefully studied by competent physiologists.

Diseases owing to the abnormally increased presence of putrefactive bacteria are not uncommon, and heretofore have not been successfully combated by the use of antiseptics. It strikes me that in copper salts we have the means of introducing a substance powerfully antiseptic towards putrefactive bacteria and probably otherwise harmless, which could be administered so as to dissolve in the alkaline mucus, secreted by the intestinal glands, while approaching the colon. Again, the antiseptic properties of the copper salts toward the sewage bacteria may be of especial benefit to the dairymen, since so many dairies are located near running streams which, through proximity to large cities, are nothing but open sewers.

October 4, 1908.

Milk from Springer cow, udders carefully washed, milked in the open, and direct in the bottles. First bottle raw, second bottle contained Miami boiler compound 1 : 2500, third bottle contained copper salt, one part copper to 250,000. The bottles were kept cold in ice-chest.

October.	Raw.	Cold boiler compound, 1 : 2500.	Copper, 1 : 250,000.
5	5'45	5'45	5'45
6	5'55	5'55	5'55
7	5'6	5'6	5'6
8	5'7	5'8	5'8
9	5'5	6'15	5'7
10	5'85	7'4	5'95
12	15'7	8'35	9'00
13	23'8	13'1	18'3
14	26'5 (a)	19'5	23'5
15	27'0	21'5	25'0
16	28'0 (b)	23'0	26'0
17	28'5	24'0	27'5
19	33'5	29'5 (c)	29'0
20	33'5	33'5 (b)	30'2
21	34'0	33'5	31'2
23	35'0	35'0	32'0
24	35'8	35'7	32'5
26	37'1	37'0	33'0 (d)
27	37'8	37'7	34'0
28	38'5	38'4	35'7 (e)

- (a) All but four turned. (c) Two of five turned.
(b) All turned. (d) One in fifteen turned.
(e) Half the bottles turned.

—*Journal of Industrial and Engineering Chemistry*, i., No. 9.

THE DETERMINATION OF TITANIUM IN ARGILLACEOUS LIMESTONES (CEMENT ROCK).

By H. M. ULLMANN and J. W. BOYER,
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THE method for the immediate determination of titanium was devised as primarily applicable to the argillaceous limestones quarried as cement rock in the Lehigh Valley district, and has been found adapted to the analysis of other limestones and to some specimens of clay.

In view of the interest that is taken at the present time in the influence on cement of elements other than those ordinarily determined, a simple, rapid, and direct estimation of titanium will hasten development of views regarding this element in finished cement. Then, too, titanium may not always be neglected in the course of routine work's analysis unless its presence in negligible quantity is first established—indeed, in the course of the present investigation, a sample of clay from a cement mill was found which contained nearly one per cent of titanium dioxide whose presence had not been suspected. A ready, direct, quantitative method of estimating this component alone, will aid in deciding whether the percentage of titanium present in any given source of supply justifies the abandonment of the determination in every routine analysis. In the course of a complete analysis, as is well known, a part of the titanium contaminates the precipitate of silica, and the remainder is precipitated with the iron and alumina.

The steps in our procedure with argillaceous and other limestones were as follows:—

1. Preliminary roasting.
2. Direct fusion with potassium pyrosulphate.
3. Solution by boiling in strong sulphuric acid, at least 1 part sulphuric acid to 4 parts water by volume.
4. Calorimetric comparisons by Weller's hydrogen peroxide method in this favourable strength of acid.

In the case of cement rock, one-half grm. of the finely ground material is heated in a platinum crucible for five minutes over a Bunsen burner, and then, for an equal time, with cover removed, over a moderate blast-lamp flame. The temperature should not be driven to a point at which the cement rock vitrifies. The necessity for this preliminary roasting is twofold—firstly, for the expulsion of carbon dioxide which would cause spattering in the subsequent fusion with potassium pyrosulphate; secondly, for the destruction of bituminous matter occurring with the rock, which if not completely burned and driven off at this point, causes serious interfering darkening and discoloration in the subsequent solution, due to the action of sulphuric acid on organic matter. A moderate blast-lamp flame is sufficient, higher temperature leading to a vitrification of cement rock and causing it to adhere to the platinum crucible and preventing its ready grinding and thorough mixing with potassium pyrosulphate.

Nothing short of grinding the roasted material in an agate mortar with pulverised potassium pyrosulphate and returning the mixture to the platinum crucible was found to yield thorough-going action. In our experiments, inasmuch as we had no difficulty with subsequent solution, potassium pyrosulphate was used, although the sodium salt might be preferable. Fusion with the pyrosulphate is initiated with a comparatively high Bunsen flame impinging on one side of the crucible, so that gases may escape through a liquid medium without causing the whole mass to lift or foam over. When the whole mass sinks into fusion, the burner is placed under the crucible with flame turned so low that a slight evolution of fumes of sulphur trioxide is just maintained. This temperature for one hour was found sufficient, two hour fusions not leading to higher results. One-half hour fusions are satisfactory, provided that the grinding with pyrosulphate is very thorough. Attempts to obtain complete solution of titanium by treatment of the roasted material with hydrochloric acid and sulphuric acid instead of fusion with pyrosulphate,

were found much more tedious and uncertain, necessitating previous vitrification of the material and long continued action and evaporation of the acids on the steam-bath.

The next step, that of solution of the pyrosulphate melt, is, as generally prescribed, a slow-going operation, requiring a solution by addition of cold water to prevent precipitation of titanium in the dilute sulphuric acid solution, and sometimes "cold" is italicised and the act of solution is prolonged for many hours, aided perhaps by stirring or by the addition of 5 per cent sulphuric acid. We found that much stronger solutions of sulphuric acid were positively beneficial for subsequent operations, and that in the act of solution they would allow us to dissolve the melt by boiling, with a gain in accuracy and at a saving of hours of time. Accordingly, the crucible and pyrosulphate melt are introduced into a beaker containing about 150 cc. of a mixture of 1 part concentrated sulphuric acid to 4 parts water by volume, *i.e.*, about 30 per cent by weight. On heating, the melt soon loosens from the crucible, the crucible and cover are removed, and the contents of the beaker heated to boiling until everything soluble is dissolved, twenty minutes being ample.

After cooling somewhat, which is hastened by standing in cold water, the contents of the beaker, soluble sulphates of titanium, iron, aluminium, calcium, magnesium, together with insoluble silica, &c., are transferred to a 200 cc. measuring flask, washing the beaker and making up to full measure with the 1 to 4 sulphuric acid. The 200 cc. volume in the measuring flask is allowed to come to room temperature, or a slightly lower temperature is preferable, as the under-cooling allows of complete separation of calcium sulphate spicules which may crystallise from the solution at room temperature and thus forestall a delayed separation later in the analysis which would lead to inopportune cloudiness. When thus cooled, the content of the flask is shaken to promote impending separation of calcium sulphate spicules, and is then poured through a dry filter, rejecting the first 10 cc., into a 100 cc. Nessler tube, until that measure is full. This solution of the unknown is now ready for comparison with solutions of known titanium content, best carried according to the colorimetric procedure of Weller, described by Hillebrand ("The Analysis of Silicate and Carbonate Rocks," *Bulletin* 305, U.S. Geological Survey).

This method consists, in the main, simply in addition of hydrogen peroxide to solutions of titanium sulphate of unknown and known content and a comparison with eventual matching of the yellow colours produced.

Our solutions of known content were prepared from the customary double fluoride of potassium and titanium, $K_2TiF_6H_2O$, which was found sufficiently pure, containing the equivalent of 30.74 per cent TiO_2 . A departure was made from the customary method of dissolving the fluoride, and, instead of evaporating nearly to dryness several times with strong sulphuric acid and dissolving in cold 5 per cent sulphuric acid, it was directly fused with potassium pyrosulphate and dissolved with boiling in 30 per cent sulphuric acid, in a manner very like the treatment of the cement rock.

The known solution is conveniently made of such strength that 1 cc. is equivalent to 0.00025 grm. TiO_2 , corresponding to 0.1 per cent TiO_2 in the 0.5 grm. sample of cement rock. An allowance may be necessary in the known solution for the very slight colour produced by ferric sulphate in the unknown. This is customarily done by matching the iron colour in the unknown with a solution of ammonium ferric sulphate in the known. We deemed it preferable to make a solution of 8.8 grms. ferrous sulphate in 30 per cent sulphuric acid and to oxidise this solution with hydrogen peroxide, finally diluting with sulphuric acid to 200 cc. In this way, any effect that hydrogen peroxide may have on the corrective iron solution is provided for. As our iron solution contains excess of hydrogen peroxide, it must, of course, be added in the proper quantity before the addition of standard titanium solution. As a rule, not more than from 2 to 3 cc. of the iron solution were required in cement

No.	Source of Sample.	TiO_2 , per cent.
1.	Alpha Portland Cement Co. Cement Rock.	
	Quarries Nos. 1 and 2, Alpha, N.J.	0.21
2.	Alpha Portland Cement Co. Cement Rock.	
	Quarry No. 3, Martin's Creek, Pa.	0.14
3.	Alpha Portland Cement Co. Cement Rock.	
	Quarry No. 4, Martin's Creek, Pa.	0.17
4.	American Portland Cement Co. Cement Rock.	
	Reliance Mill Quarry, Egypt, Pa.	0.14
5.	American Portland Cement Co. Cement Rock.	
	Giant Mill Quarry, Egypt, Pa.	0.24
6.	American Portland Cement Co. Cement Rock.	
	Central Mill Quarry, Egypt, Pa.	0.24
7.	Atlas Portland Cement Co. Cement Rock.	
	Quarry No. 1, Northampton, Pa.	0.18
8.	Atlas Portland Cement Co. Cement Rock.	
	Quarry No. 2, Northampton, Pa.	0.19
9.	Atlas Portland Cement Co. Limestone.	
	Lerch Quarry	0.11
10.	Atlas Portland Cement Co. Limestone.	
	Anneville Quarry, Anneville, Pa.	0.011
11.	Atlas Portland Cement Co. Limestone.	
	Franklin, N.J.	0.007
12.	Bath Portland Cement Co. Cement Rock.	
	Bath, Pa.	0.14
13.	Bath Portland Cement Co. Limestone.	
	Bath, Pa.	0.01
14.	Bonneville Portland Cement Co. Cement Rock.	
	Siegfrieds, Pa.	0.21
15.	Catskill Portland Cement Co. Limestone . .	0.10
16.	Dexter Portland Cement Co. Cement Rock.	
	High stone. Nazareth, Pa.	0.20
17.	Dexter Portland Cement Co. Cement Rock.	
	Low stone. Nazareth, Pa.	0.21
18.	Edison Portland Cement Co. Cement Rock.	
	Stewartsville, N.J.	0.15
19.	Hudson Portland Cement Co. Limestone.	
	Hudson, N.Y.	0.07
20.	Iola Portland Cement Co. Limestone. Iola, Kansas	0.003
21.	Lawrence Portland Cement Co. Cement Rock.	
	Creek Quarry, Siegfrieds, Pa.	0.24
22.	Lawrence Portland Cement Co. Cement Rock.	
	Canal Quarry, Siegfrieds, Pa.	0.21
23.	Lehigh Portland Cement Co. Cement Rock.	
	Quarry No. 1, Ormrod, Pa.	0.17
24.	Lehigh Portland Cement Co. Cement Rock.	
	Quarries No. 2 and No. 3, Ormrod, Pa.	0.14
25.	Lehigh Portland Cement Co. Cement Rock.	
	Quarry No. 1, West Coplay, Pa.	0.15
26.	Lehigh Portland Cement Co. Cement Rock.	
	Fogelsville, Pa.	0.18
27.	Northampton Portland Cement Co. Cement Rock.	
	Stockertown, Pa.	0.25
28.	Vulcanite Portland Cement Co. Cement Rock.	
	Quarry No. 1, Phillipsburg, Pa.	0.26
29.	Vulcanite Portland Cement Co. Cement Rock.	
	Quarry No. 2, Phillipsburg, Pa.	0.16
30.	Whitehall Portland Cement Co. Cement Rock.	
	Cementon, Pa.	0.13
31.	Bureau of Standards, Washington, D.C.	
	Standard Argillaceous Limestone.	0.226

rocks. The colour of ferric sulphate is comparatively slight at any rate, and when the greatest accuracy is not sought the correction for its colour in cement rocks may be entirely omitted.

When the iron correction factor is employed, the manipulation of the standards is:—Fill the 100 cc. Nessler tube nearly to the graduation with 30 per cent sulphuric acid, add the iron solution until the colour produced matches that of the unknown, add from a burette the known TiO_2 solution, fill to the 100 cc. mark with 30 per cent sulphuric acid, add 1 cc. commercial hydrogen peroxide free from

fluorides. With strong acid solution employed the titanium always shows its full colour reaction without danger of reversion to less coloured forms, and, furthermore, these strongly acid solutions continue to hold the titanium in solution in satisfactory condition for days, requiring only the addition of a drop or two of hydrogen peroxide from time to time.

The method as described above yields from ten to thirty determinations per day, depending on the supply of apparatus and the skill of the analyst. It may be as well to recall the fact that vanadium shows a brown colour with hydrogen peroxide which may be mistaken for titanium, or which may have a decided effect in deepening the colour produced by titanium. Considering the wide occurrence of vanadium, it is necessary to guard against this possible error in every determination. This was done by adding a drop of hydrofluoric acid to the solution of the unknown after it had been compared with the standards. If the colour developed by hydrogen peroxide is due to the titanium alone, it will be immediately discharged by the hydrofluoric acid; if due in any part to vanadium, there will remain a residual shade of colour.

The accompanying results were obtained in argillaceous limestones and other limestones representative of the Lehigh Valley cement district; and there are also included a few determinations in limestones used in other cement districts, together with a determination in the standard sample of argillaceous limestone issued by the Bureau of Standards.

Obligation is expressed to the cement companies who in all cases kindly complied with a request for samples for this investigation.—*The Chemical Engineer*, November, 1909.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, December 9th, 1909.

Sir ARCHIBALD GEIKIE, K.C.B., President in the Chair.

THE PRESIDENT announced that he had appointed as Vice-Presidents:—The Treasurer, Sir Andrew Noble, Sir James Stirling, Prof. Poulton, Prof. Lamb.

Papers were read as follows:—

"*The Hexosephosphate formed by Yeast-juice from Hexose and Phosphate*" By W. J. YOUNG.

"*Presence of Hæm-agglutinins, Hæm-opsonins, and Hæmolysins in the Blood obtained from Infectious and Non-infectious Diseases in Man.*" (Third Report). By L. S. DUDGEON, F.R.C.P. (Lond.), and H. A. F. WILSON.

These results are based upon some hundreds of experimental observations which have been made upon normal and pathological blood, and are as follows:—

1. Auto-agglutination of the red blood cells, as tested for by the methods which we have employed, may be shown to occur with specimens of pathological blood only occasionally, but never with normal blood; and auto-hæmolysis has not been met with.

2. Iso-agglutination is often met with in specimens of blood obtained from patients suffering from the same disease.

3. Hæm-agglutination is largely a specific phenomenon, both in normal and pathological blood, and the specific effect can be shown to persist even if the red cells have been subjected to high degrees of temperature or to complete drying.

4. Hæm-agglutination and bacterial agglutination are distinct phenomena.

5. Well-marked iso-hæmolysis in specimens of normal and pathological blood is not common, although some degree of hæmolysis can frequently be demonstrated.

6. Concerning phagocytosis, it would appear necessary to avoid mixing specimens of normal or pathological blood, because just as samples of sera are known to vary in value, so do the leucocytes, although to a less extent, whether they are obtained from specimens of normal or pathological blood. Still further, by mixing samples of normal or pathological blood a hæmolytic action may be induced which in itself has been found capable of exciting abnormal results in phagocytosis.

7. It appears to be incorrect to regard a specimen of blood as normal until it has been subjected to a detailed examination by the methods referred to in this and the two previous communications, quite irrespective of its actual source.

"*Gametogenesis of the Gallfly, Neuroterus lenticularis (Spathogaster baccarum).*" (Part I.) By L. DONCASTER.

"*Cell Lamination of the Cerebral Cortex of Echidna, with an Enumeration of the Fibres in the Cranial Nerves.*" By Dr. E. SCHUSTER.

"*Cortical Lamination and Localisation in the Brain of the Marmoset.*" By Dr. F. W. MOTT, F.R.S., Dr. E. SCHUSTER, and Prof. W. D. HALLIBURTON, F.R.S.

"*Caudal Fin of Fishes.*" (Preliminary Paper). By R. H. WHITEHOUSE.

"*Experiments with the Venom of Causus rhombeatus.*" By H. E. ARBUCKLE.

"*Comparative Action of Stovaine and Cocaine as Measured by their Direct Effects upon the Contractivity of Isolated Muscle.*" By Dr. V. H. VELEY, F.R.S., and Dr. A. D. WALLER, F.R.S.

As tested by an independent method, these two drugs are found to be of approximately equal physiological action in correspondence with their affinity values.

"*Glossina palpalis as a Carrier of Trypanosoma vivax in Uganda.*" By Col. Sir DAVID BRUCE, C.B., F.R.S., Captains A. E. HAMERTON and H. R. BATEMAN, R.A.M.C., and Captain F. P. MACKIE, I.M.S.

"*Critical Study of Spectral Series. Part I. The Alkalis H and He.*" By Prof. W. M. HICKS, F.R.S.

"*Distribution of the Röntgen Rays from a Focus Bulb.*" By G. W. C. KAYE, Trinity College, Cambridge.

A Röntgen bulb was constructed with an anticathode the inclination of which to the beam of cathode rays could be varied at will. The bulb as a whole was also capable of rotation, and thus by the use of a stationary ionisation chamber, intensity distribution curves could be obtained for the X-rays.

The hardness and intensity of the Röntgen rays were found to be almost independent of the obliquity of the anticathode. Some possible improvements in the modern focus bulb are suggested in the paper.

"*Direction of Motion of the Electrons ejected by the α -Particle.*" By R. D. KLEEMAN.

When an α -particle collides with a molecule, we should expect that the direction of motion of the ejected electron depends on that of the α -particle. If the whole or a part of the energy of ionisations is derived from the α -particle, the electron should have a component of motion in the same direction as the direction of motion of the α -particle. Some experiments to test this showed that when α -particles are shot through thin metal foil more electrons are given off from the side of the foil where the α -particles emerge than where they enter. This shows that the motion of the liberated electrons is on the whole in the same direction as that of the ionising α -particle.

"*Conduction of Heat through Rarefied Gases.*" By FREDERICK SODDY, M.A., and ARTHUR JOHN BERRY, B.A.

By the aid of the calcium absorption process of producing high vacua, the conductivity of twelve gases for heat has been determined at pressures so low that the actual path of the molecule is comparable with its mean free path (*cf.* Sir W. Crookes, *Proc. Roy. Soc.*, 1880, xxxi., 239). By

an electrical method the heat dissipated from a platinum strip, maintained at 61° in the gas, has been measured at various pressures down to a thermally perfect vacuum. As indicated by the kinetic theory, the heat dissipated at low pressure is proportional to the pressure, whereas at higher pressures it is independent of pressure. It was found that the conductivity in the first case bore no relation to that in the second. At all ordinary pressures, hydrogen and helium are easily the best conductors, while of the gases examined carbon dioxide was the worst. At low pressure the conductivity of acetylene, methane, and cyanogen somewhat exceeded that of hydrogen, while helium was but slightly better than carbon dioxide.

At low pressures the conductivity will be defined in terms of the calories ($\times 10^{-8}$) dissipated per second, per 0.01 mm. of pressure, per sq. cm. of surface, per 1° difference of temperature between the surface and the wall of the containing vessel. The symbols K and Q will be used to express respectively the experimental and calculated values of the conductivity so defined. On the assumption that the heat interchange between the molecule and the surface it impinges upon is perfect, Q is the product of the number of impacts of the molecules per second per sq. cm. and the specific heat of the molecule. By the aid of the kinetic theory, Q may readily be approximately calculated from the mean molecular velocity, and the molecular heat at constant volume. In the table the gases have been arranged in ascending order of K. In the second column, which gives the relative conductivity of the gas at ordinary pressures, the figures refer to the watts dissipated by the gas in the apparatus at pressures such that conductivity was independent of pressure. In the last three columns the values of K, Q, and of the ratio of K to Q, are given.

	Watts.	K.	Q.	K/Q.
Argon.. .. .	1.07	1.30	1.20	1.09
Neon	2.35	1.76	1.70	1.04
Carbon dioxide..	0.95	1.89	2.64	0.72
Oxygen	1.55	1.91	2.23	0.86
Helium	7.30	1.94	3.80	0.51
Carbon monoxide ..	1.37	1.96	2.38	0.82
Nitrous oxide .. .	0.97	2.11	2.75	0.77
Nitrogen	1.44	2.21	2.35	0.94
Hydrogen	8.75	2.29	8.95	0.25
Cyanogen	2.97	2.35	—	—
Methane	2.81	2.70	3.95	0.68
Acetylene	1.24	2.75	3.82	0.72

For argon and neon the agreement between the observed and calculated conductivity is as good as can be expected, whereas for all the other gases the ratio is less than unity, and in the case of hydrogen and helium the divergence is especially marked. The results appear to afford the means of obtaining information concerning the nature of the single impact of the gas molecule with a surface. Whereas for the denser monatomic gases the interchange of energy appears perfect, for the more rapidly moving

molecules of helium and hydrogen this is not the case. The results are preliminary, and the conclusions now tentatively suggested are being tested further with improved apparatus.

"Harmonic Tidal Constants for certain Chinese and New Zealand Ports. By T. WRIGHT.

"Photographic Action of the α -Particles emitted from Radio-active Substances." By S. KINOSHITA.

1. The photographic action of α -rays is quite distinct from that of light. There is no diminution in the action when the rays are screened by an absorbing substance, so long as they are capable of passing through the photographic film. In the case of light the action varies with the intensity of the light, which decreases on passage through an absorbing screen.

2. The photographic action of α -rays is thus independent of the velocity of the rays, and depends on the number of α -particles, N, which passes through the film, and can be expressed, when measured by the density, D, as $D = D_{\max}(1 - e^{-CN})$, where C is a constant. This formula can be theoretically deduced on the assumption that each halide grain is rendered capable of development when struck by a certain number of α -particles.

3. By counting the number of silver grains in the film exposed to a known number of α -particles, it was found that each halide grain was rendered capable of development when struck by a single α -particle.

4. The mass of silver per unit area of a developed film, calculated from the number of grains and their average size (deduced from the constant, C, in the above equation) by a consideration of the theory of probability, agrees well with the value determined from the density and the photometric constant.

5. The sensitiveness of a photographic film to α -rays cannot be characterised by its inertia. A rapid plate is more sensitive to α -rays than a slow plate, if density be taken as a criterion. The reverse holds, however, when we consider the number of grains provided, that the total amount of silver halide per unit area is the same in both cases.

6. We have now this new method of counting single α -particles, in addition to the electrical* and scintillation† methods.

The photographic method should prove very valuable for counting very small numbers of α -particles, since it is applicable to very weak sources by using very long exposures, and also to α -particles having a very short range.

"Accumulation of Helium in Geological Time." (III.). By Hon. R. J. STRUTT, F.R.S.

The present experiments refer to the amount of helium

* Rutherford and Geiger (*Proc. Roy. Soc., A*, 1908, lxxxi., 141).

† Rutherford and Geiger (*loc. cit.*); Regener (*Verh. d. D. Phys. Ges.*, 1908, x., 78; and *Sitzungsber. Kgl. Akad. Wiss., Berlin*, 1909, xxxviii., p. 948).

Locality.	Geological age.	Per grm. of zircon.			Helium ratio.
		Helium. Cc. $\times 10^{-4}$.	U ₃ O ₈ . Grms. $\times 10^{-4}$.	ThO ₂ . Grms. $\times 10^{-4}$.	
Vesuvius	Tertiary ..	< 0.2	—	—	0
Campbell Island, New Zealand	Tertiary ..	0.807	3.17	8	0.223
Mayen Eifel	Tertiary ..	1.14	12.7	0	0.090
Expailly, Auvergne	Tertiary ..	2.12	3.72	0	0.570
North East Tasmania	?	4.34	1.14	0	3.88
Brevig, Norway	Post Devonian	98.8	13.3	32.7	4.94
Cheyenne Cañon, Colorado	Palaeozoic ..	193	12.8	11.4	12.8
Green River, Henderson Co., North Carolina ..	Palaeozoic ..	255	12.9	30.1	13.4
Ural Mountains	Palaeozoic ..	300	6.34	46.5	19.0
Kimberley Diamond Mines	Palaeozoic ..	323	10.8	1.32	29.2
		210	6.57	19.8	19.8
Ceylon	Ancient.. ..	283	10.1	4.0	26.0
		575	75.3	28.5	7.1
Sebastopol, Renfrew Co., Ontario, Canada ..	Archæan ..	114	1.83	0.92	56.6

in zircon. This mineral is found in igneous rocks of all ages, and the experiments show clearly that the quantity of helium generated closely follows the geological age. This must not be taken to prove that they retain the whole of the helium generated within them by radio-active change, but rather that, as they all crystallise from fusion, they are all of similar structure, and retain a not very different fraction of the full quantity of gas in each case.

The accompanying table summarises the results. The last column shows the ratio of helium to radio-active matter (cc. per grm. of uranium oxide), thoria being reckoned as equivalent, in helium production, to 0.203 times its weight of U_3O_8 .

The Society adjourned over the Christmas Recess to Thursday, January 13, 1910.

NOTICES OF BOOKS.

Practical Chemistry for Public Schools. By A. BERESFORD RYLEY, M.A. (Oxon.). London: J. and A. Churchill. 1909.

ACCORDING as the chief aim of science teaching is the imparting of knowledge or the developing of a scientific habit of thought this book must be judged admirable or the reverse. It describes in detail all the usual chemical operations, preparations, quantitative estimations, the investigation of the properties and reactions of many inorganic substances, and some simple qualitative analysis. The methods of performing each experiment are carefully stated, equations are given throughout, and in the case of quantitative work the results of typical analyses are appended. The student is invariably told what phenomena he is to observe, and the results of each test applied, hence very little attempt is made to develop his powers of observation. The text is interleaved with blank paper, so that the student's own results may be incorporated in his practical text-book, and that he may add diagrams of apparatus or notes on any difficulties or failures. The need for systematic work in chemistry, the teaching of which has lately been in danger of becoming desultory, is recognised, and the experiments are judiciously chosen and are well within the powers of the average beginner. Volumetric analysis appears to be satisfactorily treated, and explicit directions are given for all quantitative work, the risk of failure to obtain good results being thus reduced to a minimum.

The Englishwoman's Year Book and Directory, 1910. *Who's Who Year Book*, 1910. *The Writers' and Artists' Year Book*, 1910. London: A. and C. Black.

THE first of these Year Books is now well known as an invaluable addition to the writing table of the Englishwoman of activity in any sphere of educational, literary, or scientific work. It has a value considerably above that of a mere directory, inasmuch as it contains articles by experts on subjects which are of special interest to women, and it gives sound advice relating to the choice of a profession and the prospects in various careers. The Year Book for 1910 contains many new features—sections on science, copyright, research work, and other subjects, while a short article deals with the "Position of Women in European Countries." In addition the educational section has been entirely reconstructed.

The *Who's Who Year Book* is made up of tables formerly included in *Who's Who*, and contains lists of the Professors in all the Universities in the Kingdom, of members of learned societies, of the Houses of Parliament, and many other celebrities in all walks of life. It includes also a special list of year books and directories. No biographical details are inserted, but all the information is so arranged that the Year Book is very handy for reference, and is marvellous value for its exceedingly modest price.

"The Writers' and Artists' Year Book" gives tables of British and American journals and magazines, with some details as to the character of the matter they contain, and the rate at which payment is made for contributions. It should consequently render great assistance to the author in placing his writings. Lists of literary agents and publishers are included, as well as a few hints for the guidance of inexperienced authors on such matters as the preparation of articles for the press and the correction of proofs.

The London University Guide, 1910. London: University Correspondence College.

THE candidate for any of the examinations of the University of London will do well to get a copy of this Guide, which should also be in the possession of every teacher who is preparing students for the same ordeal. It contains the regulations for all the examinations to be held in the years 1910 and 1911, an almanac of dates for application for entry forms, dates of examinations and of the publication of lists, and in addition full details of the classes and courses of the University Correspondence College, with information as to fees, text-books, &c. A short account of the history and constitution of the University is also given, together with useful advice as to the choice of a faculty, and short descriptive articles on the special subjects for 1910 and 1911.

Die Methoden zur Herstellung Kolloider Lösungen Anorganischer Stoffe. ("Methods of Preparing Colloidal Solutions of Inorganic Substances"). By Dr. THE SVEDBERG. Dresden: Theodor Steinkopff. 1909.

THIS large volume, containing nearly 500 pages of closely printed matter, deals only with methods of preparing colloidal solutions of inorganic substances, and when it is said that in every way the author is as concise as he can be without sacrificing completeness, some idea can be formed of the enormous amount of work which has been done by investigators of the chemistry of colloids. The different methods are classed as usual as condensation and dispersion methods, and the details of every experiment are given, often in the actual words of the discoverer. Absolutely no process which has been worked out is omitted, and the book is comprehensiveness itself. Excellent tabular summaries are interspersed throughout the text, and complete bibliographies are included. The type is clear, and the book is excellent both as a text-book of methods of preparing colloidal solutions and as a model of an exhaustive treatise.

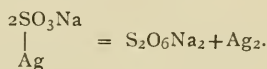
CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlix., No. 18, November 2, 1909.

Phosphides of Iron.—M. Le Chatelier and S. Wologdine.—Nine phosphides of iron have been described, viz.:— Fe_6P , Fe_4P , Fe_3P , Fe_5P_2 , Fe_2P , Fe_4P_3 , FeP , Fe_3P_4 , Fe_2P_3 . Of these Fe_6P and Fe_4P undoubtedly do not exist, the fused masses having this composition being evidently heterogeneous when examined under the microscope. The existence of Fe_3P , on the other hand, is proved by the invariability of its composition when prepared in three different ways, by the existence of a characteristic point of magnetic transformation, the existence of a maximum in the fusion curve, and by its insolubility in dilute acids and complete solubility in concentrated acids. Fe_5P_2 , described by Boblique, consists of a mixture of the two phosphides Fe_3P and Fe_2P . The existence of Fe_2P as a definite compound is proved similarly; it is, however, insoluble in concentrated acids. FeP and Fe_2P_3 also exist.

Action of Heat on Silver Sulphite and on the Double Alkaline Sulphites.—H. Baubigny.—When silver sulphite is decomposed at 100° in presence of water more than 80 per cent of it gives dithionate or hyposulphate, $2\text{SO}_3\text{Ag}_2 = \text{S}_2\text{O}_6\text{Ag}_2 + \text{Ag}_2$, and the statements that when silver sulphite precipitate is boiled with water half the silver separates as metal and the rest dissolves as sulphate are erroneous. Similarly dithionate is formed when the double sulphite of sodium and silver is boiled with water—



Berichte der Deutschen Chemischen Gesellschaft.
Vol. xlii., No. 15, 1909.

Two Lead Silicates.—L. J. Shaw and N. E. Loomis.—By the method of thermic analysis the authors have discovered the existence of two silicates of lead, viz., the orthosilicate, Pb_2SiO_4 , and the metasilicate, PbSiO_3 . The former exists in the form of colourless hexagonal tablets, which melt at 746°. The metasilicate melts at 766°.

Electrolytic Reduction of Aldehyde Ammonia in Sulphuric Acid Solution.—Peter Knudsen. The electrolytic reduction of hexamethylene tetramine in sulphuric acid solution with lead cathodes gives a mixture of mono-, di-, and tri-methylamine in varying proportions according to the experimental conditions. When formaldehyde is added only di- and tri-methylamine are formed, while in presence of ammonium sulphate the total yield of base is decreased, but the relative proportion of primary base is increased. A mixture of formaldehyde and ammonium sulphate is reduced electrolytically to amines, and a mixture of methylamine and formaldehyde in molecular proportions to dimethylamine; some methyl alcohol is also formed from the formaldehyde. Aldehyde ammonia is electrolytically reduced in acid solution, monoethylamine being the chief product, while some diethylamine is also formed. Hydrobenzamide is reduced to benzylamine and benzylidene-methylamine to benzylmethylamine.

Compounds of Antimony Pentachloride with Antimony Pentafluoride.—Otto Ruff.—Antimony pentachloride and pentafluoride form a series of six compounds as shown by the melting-point curves of mixtures of the two constituents. These compounds have the formulæ $(\text{SbF}_5)_3(\text{SbCl}_5)$, $(\text{SbF}_5)_2(\text{SbCl}_5)$, $(\text{SbF}_5)(\text{SbCl}_5)$, $(\text{SbF}_5)_2(\text{SbCl}_5)_2$, $(\text{SbF}_5)(\text{SbCl}_5)_2$, $(\text{SbF}_5)(\text{SbCl}_5)_3$; they are double compounds and not fluochlorides, and are analogous to the compounds of TiF_4 and TiCl_4 , and to such compounds as $\text{AgI}(\text{AgNO}_3)_2$. The antimony pentafluoride acts as a negative complex of about the strength of elementary chlorine, and the negative affinity of antimony pentafluoride lies between that of elementary fluorine and elementary chlorine, while the affinity of the SbCl_5 molecule is about the same as that of the bromine molecule. The author has exhaustively examined the properties and methods of preparation of the individual compounds.

Volatility of Bromides of Radium, Barium, Strontium, and Calcium.—Alfred Stock and Hans Heyne-mann.—The sublimation temperatures of the bromides of barium, strontium, and calcium at a pressure of about 0.02 mm. are as follows:—

Calcium bromide	720°
Strontium bromide	770°
Barium bromide	820°

and thus increase with the atomic weights of the metals. Hence probably radium bromide would volatilise above 900°, but the authors could not confirm this conclusion as they had no pure radium bromide. They performed three series of experiments with preparations of barium bromide containing radium bromide in various proportions, and the results showed that radium bromide is less volatile than barium bromide, and that by the partial sublimation of a

mixture of barium and radium bromides the radium salt can be concentrated in the residue. The concentrations of radium in the residue and in the sublimate are more different the smaller the amount of the latter is.

Oxidation of Iodine with Ozone.—Fr. Fichte and Franz Rohner.—The product obtained by the action of ozone on iodine has a composition which lies between that of I_2O_4 and I_4O_9 . It is not identical with Millon's I_2O_4 , and the results of analyses seem to show that most probably its composition is that expressed by the formula I_4O_9 . The substance is similar to iodine acetate in that it is very deliquescent, and is readily decomposed by water, giving iodic acid and iodine. It is apparently an iodate of trivalent iodine, $\text{I}(\text{IO}_3)_3$. When acted upon by water hydrolysis first occurs: $\text{I}(\text{IO}_3)_3 + 3\text{H}_2\text{O} = \text{I}(\text{OH})_3 + 3\text{HIO}_3$. In the second reaction iodic and hydriodic acids are formed and then react with one another, liberating iodine. The whole series of reactions may be expressed by the equation $5\text{I}_2\text{O}_9 + 9\text{H}_2\text{O} = 18\text{HIO}_3 + \text{I}_2$. Millon's yellow substance of composition I_2O_4 appears to be a basic iodine iodate, $\text{O} : \text{I}(\text{IO}_3)$.

Oxidation of Trivalent Platinum.—Lothar Wöhler and F. Martin.—On addition of ice-cold chlorine water to a dilute solution of caesium-platinum chloride, Cs_2PtCl_4 , a dark green precipitate is obtained. Its formula is Cs_2PtCl_5 . The same salt is also formed when caesium chloride solution is added to an ice-cold aqueous solution of platinum sesquichloride, PtCl_3 . The authors have not succeeded in preparing the free acid H_2PtCl_5 . CsPtCl_5 is very easily decomposed by sunlight and also by heat.

MISCELLANEOUS.

The Nitrate Trade.—Although the breaking up of the Combination for limiting the production of nitrate at the end of March this year caused a great lowering in the selling price of nitrate it has not brought about the ruinous slump that was expected; the reason being that the lower prices encouraged an extensive increase in consumption in Europe as well as, but more especially, in the United States. So much so has this been the case that in the year now closing the increased production under free conditions has not exceeded the increased consumption, and, as far as can be judged, the prospects for the new year point to a similar position, so that it is likely—if the increase in the consumption in the spring is anywhere near the amount that experts on the subject prophesy—we shall find a general rise in the price of nitrate, in which case some of the dearer producing officinas which are now closed down will be able to re-open. The weak side of Nitrate Combinations has always been that no sooner is one formed than a great number of those interested in the trade commence to finance and start new concerns, and thus damage the older officinas already in the business, and a Combination which makes no provision to prevent this only works eventually its own collapse. However, it is argued now, and with a certain amount of truth, that should another Combination be formed it will be very difficult to introduce fresh capital into the nitrate business, as the recent trouble and depression in the trade and the losses incurred will not be readily forgotten by the investing public, who will be unwilling to subscribe to fresh ventures, and this fact will leave the field to those already engaged in the business and tend to enhance the value of their factories.

MEETINGS FOR THE WEEK.

MONDAY, Jan. 3rd.—Society of Chemical Industry, 8. "Relation between the Mineral and Chemical Industries," by G. T. Holloway.

SATURDAY, Jan. 1st.	} Christmas Lectures (adapted to a juvenile auditory). "Modern Electricity," by W. Duddell, F.R.S.
TUESDAY, " 4th.	
THURSDAY, " 6th.	
SATURDAY, " 8th.	

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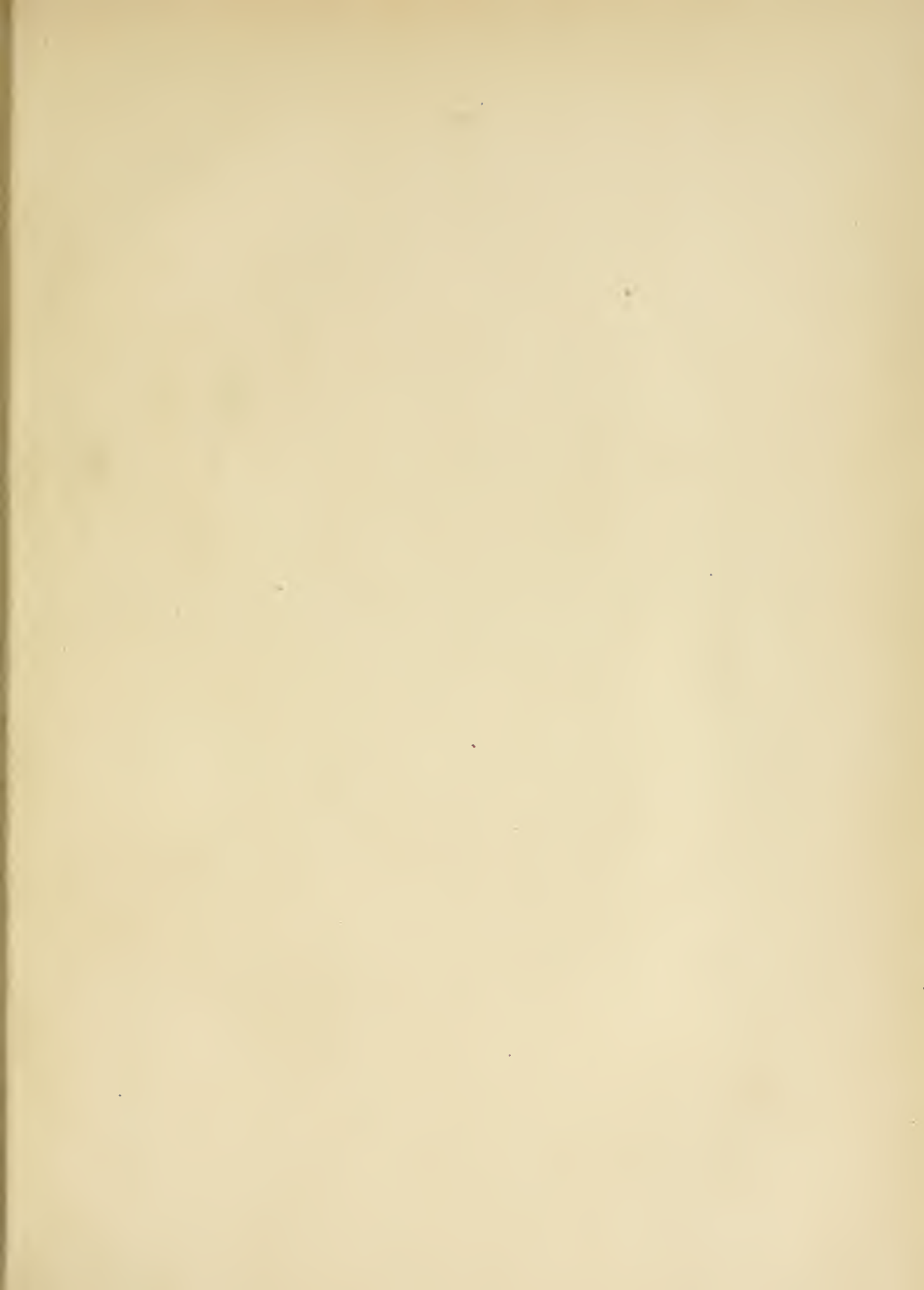
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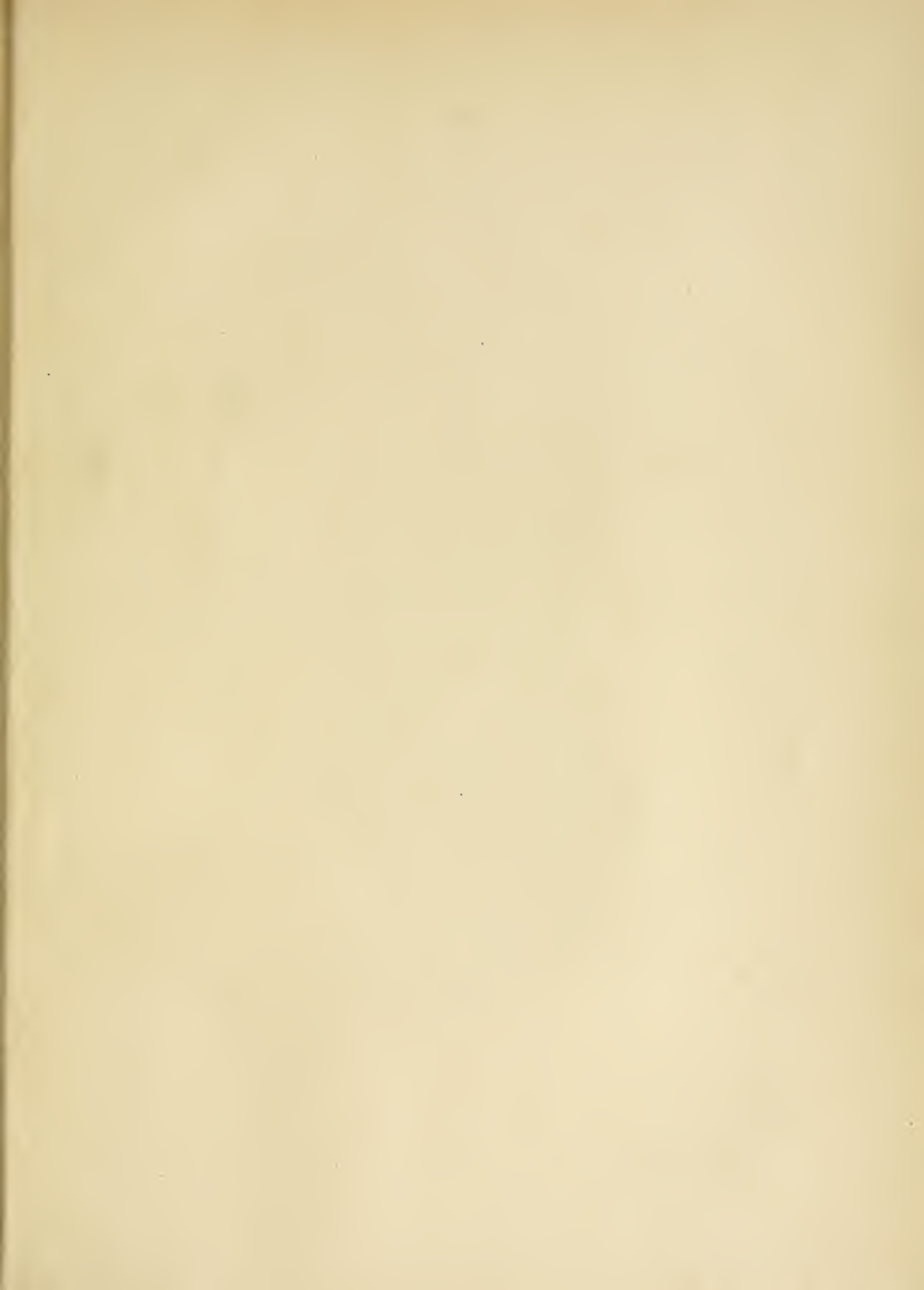
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